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SEDIMENT SAMPLING QUALITY ASSURANCE USER'S GUIDE

by

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This report is to serve as a companion to an analogous document on soil sampling quality assurance. Prior to the design of an adequate QA/QC plan for sediment sampling, there must be agreement on the objectives of the sampling program. Answers to the following questions should be available: How will the resulting data be used to draw conclusions? What actions may be taken as a result of those conclusions? What are the allowable errors in the results? Once answers to these questions are available, an experimental protocol may be prepared with an appropriate statistical design and QA/QC plan.

An overview of selected sediment models is presented to serve as a foundation for stratification of study regions and selection of locations for sampling sites, methods of sampling, and sample preparation and analyses. Discussions of situations relating to rivers, lakes, and estuaries are included.

Statistical considerations presented include experimental statistical designs to enable ANOVA to be accomplished, discussion of Type I and Type II errors, numbers and locations of sampling sites, bias, confidence and prediction limits, outliers, and testing of hypotheses. The importance of an exploratory study to the cost-effective achievement of the overall objectives of a sediment sampling program is emphasized.

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ABSTRACT

This report is intended to serve as a companion to an analogous document on soil sampling quality assurance. Prior to the design of an adequate QA/QC plan for sediment sampling there must be agreement on the objectives of the sampling program. Clear answers to the following questions should be available: How will the resulting data be used to draw conclusions? What actions may be taken as a result of those conclusions? What are the allowable errors in the results? Once answers to these questions are available an experimental protocol may be prepared with an appropriate statistical design and QA/QC plan.

An overview of selected sediment models is presented to serve as a foundation for stratification of study regions and selection of locations for sampling sites, methods of sampling, and sample preparation and analyses. Discussions of situations relating to rivers, lakes, and estuaries are included. Objectives of QA/QC plans are presented against a backdrop of objectives for sediment sampling. A suggested minimal QA/QC plan for sediment sampling is presented. In relation to different operational situations suggested guidelines are given for Type I and Type II errors and minimal relative differences from background or action levels to be detected.

Statistical considerations presented include experimental statistical designs to enable ANOVA to be accomplished, discussion of Type I and Type II errors, numbers and locations of sampling sites, bias, confidence and prediction limits, outliers, and testing of hypotheses. Some examples are given to illustrate the principles. The importance of an exploratory study to the cost-effective achievement of the overall objectives of a sediment sampling program is emphasized. A hypothetical case study related to an abandoned hazardous waste site is defined. Study objectives are presented. An exploratory study is designed, implemented and hypothetical data presented. The hypothetical data are then used to design a final more definitive study to achieve the objectives.

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CHAPTER 1

SEDIMENT SAMPLING QUALITY ASSURANCE USER'S GUIDE

INTRODUCTION

U. S. Environmental Protection Agency (USEPA) quality assurance policy requires that every monitoring and measurement project must have a written and approved quality assurance (QA) project plan (USEPA, 1980). The sixteen elements which must be contained in all QA project plans are listed below with some brief explanatory notes.

(1) Title page with provision for approval signatures.

(2) Table of Contents. (This must include a serial listing of each of the 16 QA project plan components.)

(3) Project description. (A general description of the project should be provided together with the intended end use of the acquired data.)

(4) Project organization and responsibility. (List the key individuals, including the QA officer, who are responsible for ensuring the collection of valid measurement data and the routine assessment of measurement systems for precision and accuracy.)

(5) QA objectives for measurement data in terms of precision, accuracy, completeness, representativeness, and comparability. (For each major measurement parameter list the QA objectives for precision, accuracy and completeness. All measurements must be made so that

results are representative of the media and conditions being measured.)

(6) Sampling procedures. (For each major measurement parameter(s), including all pollutant measurement systems, provide a description of the sampling procedures to be used.)

(7) Sample custody. (Where samples may be needed for legal purposes, "chain-of-custody" procedures will be used.)

(8) Calibration procedures and frequency. (Information should be provided on the calibration standards to be used and their source(s).)

(9) Analytical procedures. (Describe the analytical procedures to be used for each major measurement parameter.)

(10) Data analysis, validation and reporting. (This will include the principal criteria that will be used to validate data integrity during collection and reporting of data as well as methods used to treat outliers.)

(11) Internal quality control checks. (Examples of items to be considered include: replicates, spike samples, split samples, control charts, blanks, internal standards, span gases, quality control samples, surrogate samples, calibration standards and devices, and reagent checks.)

(12) Performance and systems audits. (Each project plan must describe the internal and external performance and systems audits which will be required to monitor the capability and performance of the total measurement system(s).)

(13) Preventive maintenance. (This should include a schedule of important preventive maintenance tasks as well as inspection activities.

(14) Specific routine procedures used to assess data precision, accuracy and completeness. (These procedures should include the equations used to calculate precision, accuracy and completeness, and the methods

used to gather data for the precision and accuracy calculations.)

(15) Corrective action. (This must include the predetermined limits for data acceptability beyond which corrective action is required as well as specific procedures for corrective action.)

(16) Quality assurance reports to management. (These reports should include a periodic assessment of measurement data accuracy, precision and completeness as well as an identification of significant QA problems and recommended solutions. USEPA, 1980)

In this report some of the factors associated with the application of these general guidelines to sediment sampling will be addressed.

BACKGROUND

This report is intended to serve as a companion to an analogous document on soil sampling quality assurance (Barth and Mason, 1984). While considerable effort is expended to make this report self-contained, it is not considered desirable to repeat all the applicable detailed discussions and explanations contained in the soil sampling report.

The most important consideration for sediment sampling, as for sampling any other media, is the objective for which the sampling is being done. The statement of objectives should contain clear answers to the following questions:

- o How will the resulting data be used to draw conclusions?
- o What actions may be taken as a result of those conclusions?
- o What are the allowable errors in the results?

Once answers to these questions are available, an appropriate statistical design for the sampling and analysis program must be devised. This statistical design should yield data from which an analysis of variance components may be done. The analysis of variance should identify components of variance associated with sampling, sample preparation, extraction, and analysis.

The statistical design of the experiment should incorporate an adequate and verifiable quality assurance/quality control (QA/QC) program for the overall study. Control is defined as the system of activities required to provide a quality product, whereas quality assurance is the system of activities required to provide assurance that the quality control system is performing adequately. It cannot be overemphasized that an adequate QA/QC program cannot be tailored for a study until a clear statement of monitoring objectives, together with allowable errors, has been provided.

Often actions may not be taken on the basis of monitoring measurements in a single medium such as sediments. If one is concerned about risks to human health or the environment, for example, concentrations of hazardous substances in sediments may not provide sufficient information on which to base the magnitude and extent of necessary control actions. For such a risk analysis it may be necessary in addition to measure concentrations of hazardous substances in surface waters, groundwater, and foodstuffs to obtain some measure of the biological availability of the hazardous substances in sediments which can be related to potential exposures via various routes. In cases in which sediment sampling is only a part of the total monitoring program, it is mandatory to modify the QA/QC program to cover all aspects of the total program to ensure that the total combined errors in the final results will not exceed allowable errors (McNelis et al., 1984).

Prior to engaging in a more detailed discussion of QA/QC aspects for sediment sampling, it is desirable to present and discuss some possible sediment monitoring objectives. Objectives of sediment sampling may include:

- Determining the extent to which sediments act as either sources or sinks for water pollutants,
- Determining presence and distribution of selected pollutants in sediments in both space and time,
- Determining the risk to human health and the environment from sediment contamination by selected pollutants, and
- Obtaining measurements for validation of sediment transport and deposition models.

Further discussion of these objectives in Chapter 3 includes some hypothetical examples related to different environmental protection laws.

To establish an adequate, cost-effective QA/QC plan for a sediment monitoring program, it is necessary for a decision-making official after careful analysis of the consequences, to specify allowable Type I and Type II errors in reaching conclusions based on sample data. A Type I error, for a situation in which a measured population mean is being compared to either an action level or a control level, is committed when it is concluded that the population mean exceeds the action or control level when in fact it does not. For the same situation, a Type II error is committed when it is concluded that the population mean does not exceed the action or control level when in fact it does. See Chapter 4 for additional discussion of Type I and Type II errors. The political, social, and economic consequences of making either a Type I or Type II error must be weighed before a decision-making official can establish allowable frequencies for each type error.

OBJECTIVES

This document is intended to serve as a user's guide that identifies and explains selected principles and applications of the methods and procedures for establishing an adequate QA/QC program for sediment sampling aspects of environmental monitoring programs. It is not intended to serve as a guide for identifying all sediment sampling equipment or to serve as a sediment sampling protocol. Similarly, it is not intended to provide "cook book" type details for the development and implementation of a universal QA/QC plan for all sediment monitoring programs. The goal is to provide a flexible, but technically sound, framework within which the user can devise a QA/QC plan consistent with the specific objectives of any sediment monitoring program.

No detailed treatment of analytical quality assurance procedures is given since that important aspect of the overall problem has been adequately treated elsewhere (USEPA, 1982; USEPA, 1984). It should be noted, however, that in a QA/QC sense sampling procedures are not fully separable from analytical procedures. This is particularly true for sample collection and handling procedures. Thus, sediment sampling QA/QC procedures presented here should be viewed as important integral elements of the overall QA/QC plan.

AUDIENCE

This document has been developed to serve as a user's guide for anyone designing, implementing, or overseeing sediment monitoring programs. It is especially applicable for personnel responsible for regulatory programs involving sediment monitoring. Special attention is given to sediment sampling examples related to CERCLA since such applications are deemed of high priority for sediment sampling programs. Many of the principles and procedures discussed, however, are applicable to other situations as well.

APPROACH

In Chapter 2 a brief overview of models describing the dynamics of sedimentation in different bodies of water is presented. Knowledge of sediment dynamics provides a firmer foundation for the design of sediment monitoring programs and associated QA/QC plans and assists in the interpretation and evaluation of the resulting data. Chapter 3 provides examples of some hypothetical sediment monitoring situations together with discussions of required QA/QC plans. Chapter 4 contains selected applicable statistical methodology.

The role of an exploratory or preliminary study prior to the performance of the definitive study is described in Chapter 5. Chapter 6 describes how to determine for the final definitive study the required number of sediment samples and sampling sites consistent with established allowable probabilities for Type I and Type II errors and the desired minimum detectable difference between means and either control levels or action levels. Chapter 6 also discusses sediment sample collection, sample handling, and analysis and interpretation of QA/QC data.

The subjects of systems audits and training are not addressed in this document. The treatment of these subjects in the companion volume (Barth and Mason, 1984) is considered to be equally applicable to sediment sampling. In order to make this report more self-contained, the entire chapters on sample handling and documentation, analysis and interpretation of QA/QC data, and systems audits and training from the companion soil document are included in Appendices B, C and D, respectively.

CHAPTER 2

MODELING SEDIMENT TRANSPORT AND DEPOSITION

INTRODUCTION

In determining the appropriate model to use in describing the role of sediments in the transport and fate of hazardous substances, one must have a definition of sediments along with site-specific characteristics for sites of interest. For areas of concern, i.e., rivers, lakes, and estuaries, sediments and related data of importance will have general (geological strata, soil type, climate, etc.) as well as specific (flow rate, bed load, water pH, etc.) characteristics. The term sediment is defined as any particulate matter which can be moved by water, to or from a land surface and into or through the waterways of a river basin, a lake system or an estuary (Leytham and Johanson, 1979). Particulate sediment matter is usually partially made up of once-living organic material in various degrees of decomposition with particle sizes ranging from colloidal humus to large pieces of material. Sediments normally contain some mineral particles. These may include any of the three major rock types: igneous, metamorphic or sedimentary rocks. The size of these particles can range from that of clays through silts and sands to large boulders. A size classification scheme has been developed by Wentworth and is shown in Table 1.

Total sediments are the sum of suspended and bed-load sediments. Suspended sediments occur mainly in slower moving waters of sluggish rivers, lakes and estuaries. Suspended sediments may have more long-term adverse effects on ecosystems

Table 1. WENTWORTH PARTICLE SIZE SCALE

Limiting particle diameter					
mm	φ units	µm		Size class	
2048	−11		Very large	Boulders	GRAVEL
1024	−10		Large		
512	−9		Medium		
256	−8		Small		
128	−7		Large	Cobbles	
64	−6		Small		
32	−5		Very coarse	Pebbles	
16	−4		Coarse		
8	−3		Medium		
4	−2		Fine		
2	−1		Very fine	Granules	
1	0		Very coarse	Sand	
1/2	+1	500	Coarse		
1/4	+2	250	Medium		
1/8	+3	125	Fine		
1/16	+4	62	Very fine		
1/32	+5	31	Very coarse	Silt	MUD
1/64	+6	16	Coarse		
1/128	+7	8	Medium		
1/256	+8	4	Fine		
1/512	+9	2	Very fine		
				Clay	

Source: Davis, 1983

than bed-load sediments. These sediments can increase turbidity of the water and therefore decrease sunlight availability to the primary producers, as well as limit visibility of predators. They can also clog filtering devices of molluscs and fish (Farnesworth, et al., 1979).

Bed-load sediments are more significant in the faster moving waters of river systems. These sediments can scour, abrade and bury all or part of the benthic organisms, thus modifying the food chain (Farnesworth, et al., 1979). They can even modify the habitat structure. The effects of sediments in general can be propagated throughout an ecosystem and may result in the mass movement of organisms out of an area. This is not to say sediments are always negative factors to an ecosystem; sediments may carry nutrients into an area, thereby increasing biological productivity. Most negative sediment impacts are observed after runoff episodes associated with storms or snow melt.

Sediments may readily adsorb pollutants. The dynamics of pollutant movement on adsorbed sediment are not well understood; however, research is ongoing to elucidate such transport. Some of the factors involved include concentration of the dissolved pollutants, flow velocity of the water, kinetic adsorption coefficients, and depth of flow (Krenkel and Novotny, 1980).

The process of adsorption-desorption of pollutants on sediments has a direct effect on the transport processes and on the bioavailability of the pollutants (OECD, 1981). Sediments will have varying reaction phases with pollutants, depending upon the sediment's chemical makeup and certain environmental factors (temperature, pressure, water flow rate, etc.).

TRANSPORT AND SEDIMENTATION

The first factor to consider is the texture of the sediments. Sediment texture has a number of characteristics.

Particle size of the sediments is important; sediments can either be homogeneous or heterogeneous with regard to particle size. The particle's shape and surface characteristics are important in determining whether and to what extent pollutants are adsorbed. Porosity and permeability are two important properties of sediments.

Sedimentation processes include: 1) Biological processes, 2) Organism-enhanced sedimentation and 3) Physical processes. In biological processes, two important factors predominate. They are degradation, which is the working and reworking of the sediment by biological organisms, and pelletization, which is the accumulation of biological excrement. In organism-enhanced sedimentation, it is the bottom-rooted plant life that promotes trapping and deposition of sediments. Physical processes are by far the most important. These include in particular fluid flow characteristics in relation to the settling of different type and size particle. In fluid flow, there are two different types of flow: 1) laminar flow and 2) turbulent flow. Either the Reynold's number or Froude's number may be used to characterize the flow as laminar or turbulent (Davis, 1983).

Stoke's Law of settling identifies and relates the different variables involved in the settling of particles (Davis, 1983). Unfortunately, Stoke's Law tends to be valid for only a single particle, and concentrations of sediment tend to retard the total settling.

For a specific sized particle of a specific shape and density, there is a minimum fluid velocity needed to move that particle. This minimum velocity is known as the threshold velocity. There are several important mechanisms involved in the movement of sediment particles in fluids. Traction defines the mechanism whereby particles may slide or roll over the substrate, and is particularly important on the bottom where particles are in contact with one another. Saltation is transport whereby the grains bounce or hop along the substrate and it usually accompanies traction processes. Both traction and saltation processes contribute to the bed load. Bed load may be defined as the sediment load that moves by traction and/or saltation along the bed as the result of shearing at the boundary of flow (Davis, 1983). Suspended sediment load is comprised of particles in the main flow of the current that move significant distances without contact with the bottom or side substrata. Maximum transport of sediments occurs mainly during turbulent flow, such as that which occurs during storm or snow-melt periods.

The sediment texture (or particle size distribution) is directly related to the hydraulics of the system. The most prominent cause contributing to observed sediment texture is a change in the competence or capacity of a stream, which causes sediment particles to come to rest. The coarsest particles are present in the traction population of sediments. The saltation sediment population contains the bulk of the sediments with the particles therein being well sorted. The sorting is due to the differential efficiencies of continued suspension and redeposition while particles bound along. The suspended load of a sediment sample shows considerable variation due to both the intensity of turbulence and the original characteristics of source sediments, such as cohesion and flocculation. Sorting within this population is poor.

Turbidity currents occur when fluid turbulence causes sediments to become suspended. Turbidity currents can occur in deltaic regions and also in estuaries. Liquified sediment flows occur when sediment is supported by upward-flowing fluid as particles settle. Debris flows are a mixture of fine sediments and fluid which support larger particles. These usually occur off mountain sides. A slump occurs when masses of soil move along shear planes. These often occur on the sides of rivers and also are types of "mud" flows.

Rivers

Two main types of rivers are found in the world today. One type, the braided stream (stream will be used synonymously with river), is or has been a predecessor to the second, the meandering stream.

A braided stream has numerous channels that are separated by bars and small islands. The deposition of sediment is characterized by the shifting of the channels and bar aggradation. These types of streams have an overabundance of sediments. Streams are braided due to the inability of the stream to move the coarse component of its load (Davis, 1983). However, during floods, all sized particles are moved. There are four types of events in which sedimentation occurs in braided streams: 1) flooding, 2) lateral accretion - side or point bars develop, 3) channel aggradation - due to the waning energy of the stream and 4) reoccupation of an older channel causing cut and fill. Examples of braided streams include the Trollhiem River in California, the Platte River in Nebraska and the Bijou Creek in Colorado. Models (geologic) have been based on these rivers. Figure 1 shows a block diagram of this type of stream.

A meandering stream is a single channeled stream that displays a relatively ordered condition of riverine and sediment accumulation processes. These are commonly situated downstream from braided streams. They lack gravel, have a modest suspended load and have a broadly meandering pattern. These types of streams are commonly found on coastal plain regions flowing more or less perpendicular to the coast. They have specific sedimentary deposits such as levees, floodplain and point bar deposits. These streams are characterized by turbulent flow, and sediment is transported in both bed load and suspended load. Sediment is commonly eroded from one bank and accreted on another downstream. Examples of meandering

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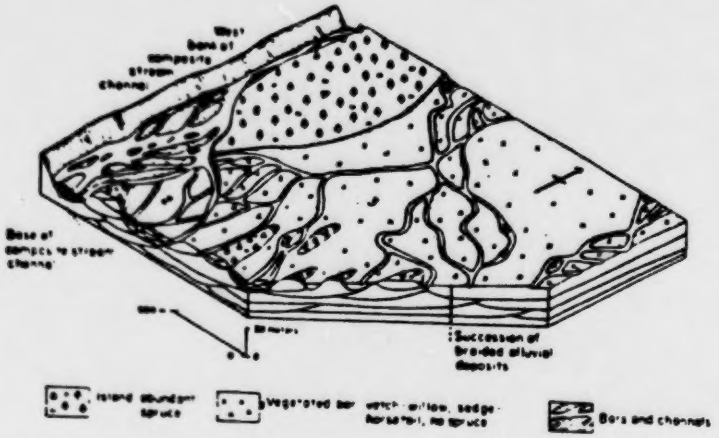
West
bank of
composite
stream
channel
Base of
composite stream
channel
Succession of
braided alluvial
deposits
Island abundant
spruce
Vegetated bar: vetch, willow, sedge,
horsetail, no spruce
Bars and channels

Figure 1. Block diagram of a braided stream and adjacent environments. Source: Davis, 1983,
After Williams and Rust, 1969

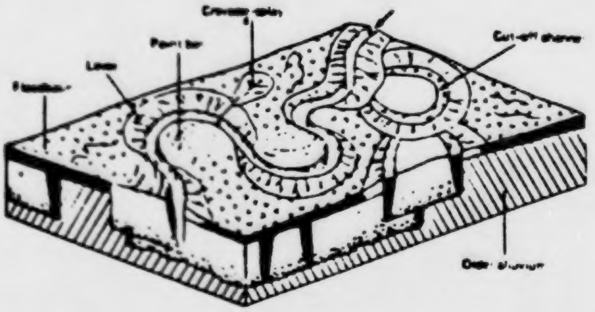
Crevasse splay
Point bar
Levee
Floodbasin
Cut-off channel
Older alluvium

Figure 2. Block diagram of a meandering stream showing major depositional environment. Source: Davis, 1983

streams are the Mississippi River, the Ohio River, and the Colorado River. The Colorado is an excellent example of a braided stream becoming a meandering stream. Figure 2 is a block diagram of this stream type.

Deltas are accumulations of sediment at the end of a river channel where it discharges into a standing body of water. Deltas can occur in oceans, lakes and estuaries. Erosion of a delta can be dominant at times, with the primary agents being waves and/or currents. The processes that act upon a marine delta are riverine processes and marine processes.

In riverine processes, three primary forces are generally dominant: 1) inertia, 2) bed friction and 3) buoyancy. Circumstances leading to the formation of deltas occur in lakes, estuaries, and enclosed seas in which there are broad, flat, offshore slopes.

In marine processes there are three dominant forces: 1) tides, 2) waves, and 3) coastal currents. The Mississippi delta is a major example for which a model has been developed.

Lakes

Lakes occur throughout most climatic belts of the world and receive large volumes of sediments. Most lake studies emphasize the biological, chemical and physical aspects of the environment. Only relatively recently have lake sediments been given the major consideration due them.

Depending upon a variety of environmental factors, lakes may stratify in the summer and in the winter. Figure 3 illustrates the process and the mechanism whereby mixing may occur in spring and fall months.

The Great Lakes are so large that the circulation caused by the cooling and sinking of maximum density water, which is replaced by deeper water, is not sufficient to cool the whole

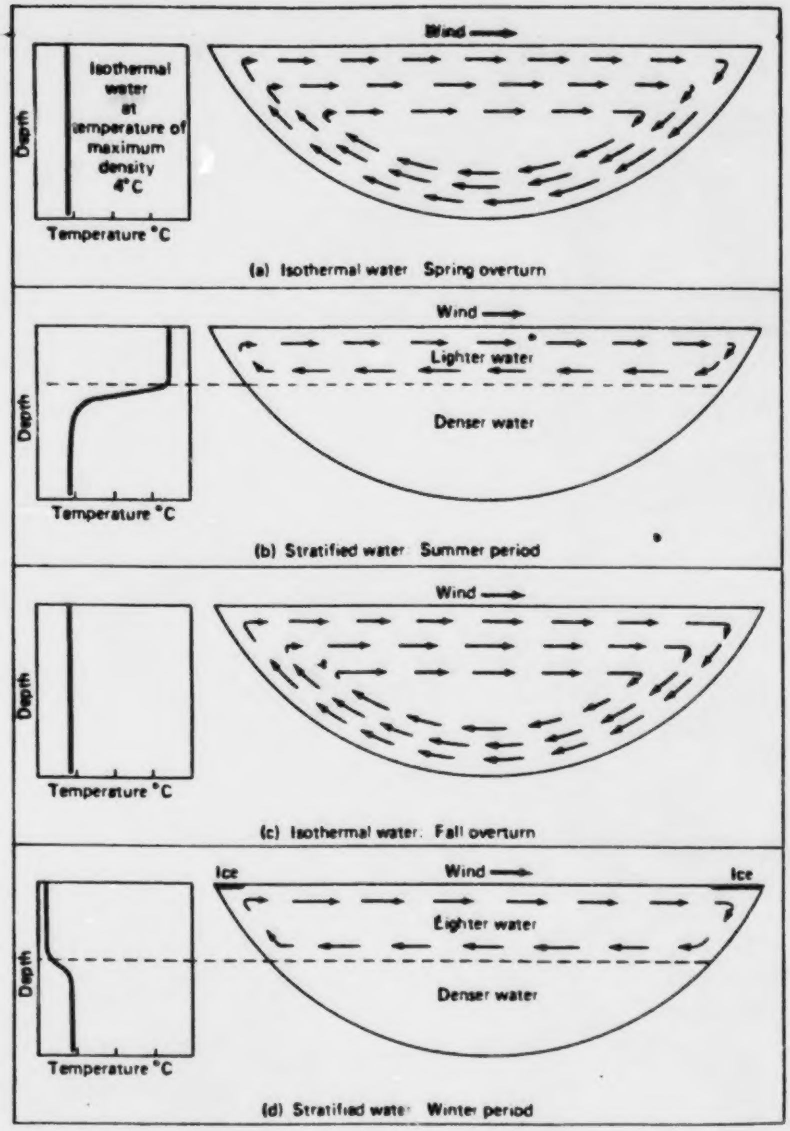
Wind
Isothermal water at temperature of maximum density 4°C
Depth
Temperature °C
(a) Isothermal water Spring overturn
Wind
Lighter water
Denser water
Depth
Temperature °C
(b) Stratified water Summer period
Wind
Depth
Temperature °C
(c) Isothermal water. Fall overturn
Ice
Wind
Ice
Lighter water
Denser water
Depth
Temperature °C
(d) Stratified water Winter period

Figure 3. Four stage diagram showing stratification and and overturn periods for a dimictic lake.

Source: Davis, 1983, After: Hough, 1958

lake body to maximum density, and hence they never completely freeze over (Garrels et al., 1975). Stratification in large lakes such as the Great Lakes occurs only in the summer.

During stratification, if enough organic material exists in deep water, oxygen can disappear completely. This produces changes in the bottom fauna and promotes production of gases such as hydrogen sulfide (H_2S) and methane (CH_4). Shallow lakes are stirred by wind and waves, thereby minimizing stratification, but lakes of intermediate depth are very susceptible to stratification and oxygen deficiency. Excessive plant nutrients promote plant macrophyte growth which aids in the deoxygenation process in small lakes by reducing wave action and thus mixing. This can lead to a lake being overwhelmed by organic material.

There are two main types of sediments other than organic material found in lakes. One, terrigenous sediments, can originate from two main sources, either from the edge of the lake itself or from being transported in by other means, i.e., rivers and waste water. The second sediment type is composed of chemical precipitates and comes from the water constituents themselves. There are two categories of lakes based on their chemical constituencies: 1) saline lakes and 2) carbonate lakes. Waste water can add chemicals to the water of either category and form various types of precipitates.

Estuaries

There is a wide variety of morphology, hydrodynamics and sediment distribution in estuaries. Four main morphological types of estuaries are known: 1) drowned river valleys, 2) fjords, 3) bar-built estuaries and 4) tectonically produced estuaries. Widely distributed, irregularly shaped estuaries are common along coastal plains as a result of drowned river valleys from the sea level rising in the Holocene period. Chesapeake Bay and Delaware Bay are examples of this type. This estuary type is characterized by rapid sediment accumulation. Fjords are deep, steep-sided estuaries carved by glaciers and are characterized by poor circulation and slow sediment accumulation. Fjords tend to be small and are typically developed on tectonically active coasts. As estuaries develop and coastal processes transport sediment along, it is common to develop spits and barriers that can partially or completely close the mouth of the estuary, with tidal inlets interrupting an otherwise continuous barrier. The large estuaries behind the outer banks of North Carolina represent this type. Tectonically produced estuaries are generally confined to leading-edge coasts where faulting and subsidence create embayments. San Francisco Bay is such an estuary (Davis, 1983).

Two main processes are found to be of great importance to sediment accumulation in estuaries. Tidal currents, which constitute the first process, are directly related to tidal range in most instances. The size of the inlet into an estuary is also important, as well as the speed of the current into and out of the inlet. Sediment from freshwater runoff as well as from oceanic processes must be considered. A sudden decrease in the current speed at the landward or seaward side can cause rapid accumulation of sediment. Riverine processes constitute the second main factor contributing to sediment accumulation. Since an estuary is a standing body of water, a delta can form at a river's mouth. If the tidal currents are not sufficient to remove the sediment, accumulation occurs. It is due to these two processes that estuaries are generally short-lived geologically.

Estuary circulation is primarily based upon the zone in which freshwater comes into contact with seawater. There are three estuary types based upon the nature and distribution of this zone. A highly stratified or salt wedge estuary is one in which there is little mixing of the waters and a density stratification occurs. River discharge must be the dominant process in the formation of this estuary (Pritchard, 1955). Mixing only occurs by vertical advection in the shear zone between the two opposing masses (Biggs, 1978). Sediment carried to the estuary from the stream may settle into the salt-wedge layer and be transported to the landward tip for deposition. Well-stratified estuaries display a complicated circulation which is related to the Coriolis effect. During flood tides, the interface of the water masses is tilted up on the right side of the estuary in the northern hemisphere as one looks landward, and in ebb tide it is tilted to the left side (Davis, 1983). This results in a circular flow component in which the center is a null point. Partially mixed estuaries are ones in which tidal influence is dominant in determining circulation and mixing of waters. Turbulence created by tidal action causes downward movement of freshwater as well as upward movement of seawater (Pritchard, 1955). This results in a gradual increase of salinity from top to bottom. Suspended sediment tends to concentrate in the area of maximum turbidity which is located just downstream from the landward limit of seawater intrusion. When riverine and tidal processes are equal in importance, a totally mixed estuary will result. The Coriolis effect also plays a role in circulation and sedimentation of these estuaries. These estuaries are vertically homogeneous. Sediment will follow the pattern provided by the Coriolis effect with marine sediments concentrating on the right (looking landward from the sea), and river sediments concentrating on the left (Biggs, 1978).

The models reviewed in the next section will demonstrate general principles and how they apply to sediment sampling. Few models are based on the sediments alone; most include the system as a whole.

MODELING THEORIES

Mathematical models of systems are often a useful method of generating and evaluating the various outcomes. A model, however, should not be considered valid until it has been substantiated by field and/or laboratory measurements (Krenkel and Novotny, 1980). Table 2 presents an overview of some commonly used models. The range and choice of available models is clearly quite broad.

The following guidelines have been taken from Grimsrud et al., 1976 on the selection and use of models:

1) Define the problem and determine what information is needed and what questions must be answered.

2) Use the simplest methods that can provide the answers to your questions.

3) Use the simplest models that will yield adequate accuracy.

4) Do not try to fit the problem to a model but select a model to fit the problem.

5) Do not confuse complexity with accuracy.

6) Always question whether increased accuracy is worth the increased cost and effort.

7) Do not forget the assumptions underlying the model used, and do not read more significance into the simulation results than are actually there.

Stream (river) as well as lake and estuary models tend to be based upon a one-dimensional approximation of the flow, momentum and mass conservation equations. These models put more emphasis on convective transport of pollutants than on dispersion. The models range from simple, steady state, dissolved oxygen relationships to very complex models describing the interrelationships among pollutant additions and removals, organic matter concentrations, and life processes occurring in aquatic environments (Krenkel and Novotny, 1980).

Table 2. Overview of Selected Water Quality Models

Model	Developer and/ or Source*	Model Category	Model Characterization	Processes Included	Parameters Modeled	Input Data and Computer Requirements
HSP-II	Hydrocomp International	overland hydrologic watershed model	dynamic	runoff, pollutants, pickup and transport	flow, sediment, most of water quality parameters	large
SWMM	Metcalf and Eddy, U. of Florida Water Res. Eng	overland surface runoff from isolated storms	dynamic	runoff, erosion, pollutant pickup and transport	flow, sediment, most of water quality parameters	large
STORM	Wat. Res. Eng United States Army Corps of Engineers	overland surface runoff	quasi-dynamic	surface runoff, erosion poll. pickup	flow sediment, sediment adsorbed poll	medium
LANDRUN	Marquette U., Wisc DNR	overland runoff	dynamic	runoff, erosion, pollut. pickup and routing	flow, sediment, sediment adsorbed pollutants	medium
DOSAG	Texas Wat. Dev. Board	stream	steady state	deoxygenation reaeration nitrification	D. Oxygen, nitrogen	small
QUAL-II	EPA	steam	semi-dynamic	stream pollutant transport	D. Oxygen, temperature, most of water quality parameters	medium
SWMM-RECEIV	Wat. Res. Eng., EPA	stream	dynamic	stream pollutant transport	D. Oxygen, nitrogen, conservative pollutants	large
HSP-II CHANNEL QUALITY	Hydrocomp International	stream	dynamic	stream pollutant transport	D. Oxygen, nitrogen, conservative pollutant transport	large
M.I.T. Network Model	M.I.T	stream, estuary	dynamic	pollutants transport, eutrophication, nitrification	D. Oxygen, nitrogen, conservative pollutants, temperature	large
M.I.T. Reservoir Model	M.I.T	deep reservoir	dynamic	stratification, thermal balance, mass transfer	temperature, dissolved oxygen	large
Chen and Orlob Model	Wat. Res. Eng	stratified estuary, lake or reservoir	dynamic	pollutants and energy balance, eutrophication	temperature, oxygen, most of wat. quality parameters	large
PLUME	Pac. Northwest, EPA	mixing zone	steady state	buoyant jet and plume mixing	conservative pollutant	medium

*Hydrocomp International, Palo Alto, Ca.
Metcalf and Eddy, Boston, Mass
Water Resources Engineers, Walnut Creek, Ca
Marquette University, Dept. of Civil Engineering, Milwaukee, Wisc
Dept. of Natural Resources, Madison, Wisc.
University of Florida, Dept. of Environmental Eng. Sci., Gainesville, Fla
Texas Water Development Board, Austin, TX
Massachusetts Institute of Technology, Dept. of Civil Engineering, Cambridge, Mass.

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Source: Krenkel and Novotny, 1980

Sediments in some instances are considered pollutants. Discharge limitations have been imposed for suspended solids. Many pollutants can be transported in suspended solid form or adsorbed on suspended particulates. Unfortunately, the dynamics of the movement of pollutants adsorbed on sediments is not well understood.

The description and solution of the hydrodynamic behavior of surface or groundwater systems are essential parts of every water quality model. Basic hydrodynamic laws which must be included in descriptions of water quality systems are: 1) the water conservation equation (the equation of continuity) and 2) the momentum conservation equation (equation of motion) (Krenkel and Novotny, 1980). The water conservation equation states that the difference of the flow entering and leaving a control volume must equal the rate of storage in the volume. The applicable partial differential equation is:

$$\frac{\partial A}{\partial t} + \frac{\partial Q}{\partial x} = q_i$$

where

A is the cross-sectional area

t is time

Q is the flow

x is the direction of flow

q_i is the lateral inflow into the control volume per unit path length in the direction of flow.

If one multiplies each term in this equation by a unit of path length in the direction of flow, it can be seen that $\frac{\partial A}{\partial t}$ represents rate of storage, $\frac{\partial Q}{\partial x}$ outflow rate, and q_i lateral inflow rate; or, rate of storage = lateral inflow rate - outflow rate.

The momentum conservation equation is based upon Newton's second law of motion which states that the rate of change of momentum equals the sum of external forces acting on the control volume. The applicable partial differential equation is as follows:

$$\frac{\partial}{\partial t}(UH) + \frac{\partial}{\partial x}[(U)\ (UH)] + gH\frac{\partial H}{x} = gH(S_o - S_f)$$

where

U is flow velocity
t is time
x is the direction of flow
g is gravity acceleration
H is the depth
S_o is the bottom slope
S_f is the energy (friction) slope of the flow (may be obtained from semiempirical flow formulas)

If one multiplies each term of the equation above by the water density ρ and Δx, the terms in the equation have the following meaning:

$\frac{\partial}{\partial t}(\rho UH)\,\Delta x$ = rate of change of momentum in a control volume

$\rho\frac{\partial}{\partial x}[(U)(UH)]\Delta x$ = difference between rate of momentum entering and that leaving a control volume

$\rho gH\frac{\partial H}{\partial x}\,\Delta x$ = net hydrostatic pressure of the surrounding water on the control volume

$\rho gHS_o\,\Delta x$ = gravity force due to the weight of the control volume

$\rho gHS_f\,\Delta x$ = friction shear resistance force

In words, the equation states that for a control volume of water the difference between the rate of momentum entering and leaving plus the rate of change of momentum inside the control volume is equal to the sum of the external forces acting on the control volume.

Suspended particles originate from soil erosion, bank erosion, urban solids, washload and organic life processes (Krenkel and Novotny, 1980). The channel phase of sediment transport can be divided into the suspended fraction and the fraction of sediments contained by moving streambeds. In suspended sediment transport analysis, it is important to determine where and when a particle will settle or when and where the bed particles will be resuspended. Stoke's Law is the general basis for sedimentation.

The equations of continuity and motion remain the same in any sediment transport model. The mass balance equation for pollutants (i.e., phosphorous, heavy metals, adsorbed pesticides) must be coupled with sediment transport since adsorption or release may take place between the adsorbed and dissolved pollutant phases. The adsorbed component moves with the sediment and is therefore subject to any processes that may influence the sediment. The exchange of matter between the bottom deposits and overlying water is governed by adsorption equilibrium and limited by the diffusion velocity through the bottom boundary layer. Two phases described when giving general mass balance equations for adsorbed pollutant movement are the free phase and the sorbed phase. The coupled equations for each are as follows (Krenkel and Novotny, 1980):

Free phase: $$\frac{\partial C}{\partial t} = -U \frac{\partial C}{\partial x} - \rho \frac{\partial S}{\partial t} \pm \Sigma N - K_d C$$

Sorbed phase: $$\frac{\partial S}{\partial t} \simeq K_s(S_e - S) - K_{ss}S + M)/H$$

where

C is the concentration of the dissolved pollutant (mg/liter)

S is the concentration of the adsorbed pollutant (μg/g of suspended solids)

S_e is the adsorption equilibrium concentration of the pollutant (μg/g of suspended solids) described by an isotherm

U is the flow velocity (m/day)

is the specific density of the particulate matter (g/cm^3)

N is the sum of the sinks and sources (g/m^3/day of the substrate which includes uptake of the phytoplankton, transformation into another form, diffusion into or from benthal layers, etc.)

K_d is the decay coefficient describing the loss of substance from the system (day^{-1})

K_{SS} is the settling rate of the substance (m/day)

K_s is the kinetic adsorption coefficient (day^{-1})

M is the scour rate of the pollutant adsorbed on the sediment from contact with the bottom deposits (g/m^2/day)

H is the depth of flow (m)

x is the distance (m)

t is the time (days)

In words the equation for the free phase states that the rate of change in concentration of a dissolved pollutant =

rate of loss by flow (convective transport) + rate of loss to adsorption on suspended solids + rate of gains or losses from sources or sinks respectively + rate of loss of the pollutant from the system by processes not otherwise accounted for

In words, the equation for the sorbed phase states that the rate of change in concentration of the pollutant adsorbed on suspended solids ≃

Rate of gain of adsorption (driven by the difference between the adsorption equilibrium concentration and the actual adsorption concentration) + Rate of loss due to settling + rate of loss due to the scour rate of the pollutant adsorbed on the sediments.

Use of the cited equations plus others is very important when developing a model of sediment/pollutant relationships. The development of the CHANL model by the U.S. Environmental Protection Agency (USEPA) has demonstrated the process.

The basic equations of any model must all be defined. Also, exact definition of the solution being sought is needed before an appropriate model can be selected to solve the problem.

CONCLUSIONS

When using or developing mathematical models all the parameters must be chosen carefully. Sediment, in this case, is very important but is linked to many other parameters. Knowledge of these parameters is imperative when deciding which model is to be used and how the results will be displayed.

Sediment plays an important role in the transport of pollutants as well as in the transport of nutrients. Both the pollution and nutrient aspects must be considered. Sediments can overwhelm bottom fauna, but the nutrients they carry can give rise to new biota. By the same token, sediments can transport pollutants that are hazardous to some life forms of a particular waterway.

In choosing an appropriate model, a comparison should be made of available models. A model must be fitted to the problem and action taken accordingly. Many good models exist, but only the ones which contain sediment factors will be adequate for our needs here.

CHAPTER 3

OBJECTIVES OF QUALITY ASSURANCE-QUALITY CONTROL PLANS

INTRODUCTION

USEPA Order 5360.1 establishes the responsibilities of National Program Managers in the Agency's Mandatory Quality Assurance Program. These responsibilities include ensuring that "data quality acceptance criteria" and QA Project Plans are prepared for all data collection projects sponsored by the office. In a memorandum of April 17, 1984 accompanying the issuance of Order 5360.1, Deputy Administrator Alm identified two steps that must be taken to ensure that all data collected by USEPA are suitable for their intended use:

"...the user must first specify the quality of data he needs; then the degree of quality control necessary to assure that the resultant data satisfy his specifications must be determined."

The first step is accomplished through the development of Data Quality Objectives (DQOs). Data Quality Objectives are qualitative and quantitative statements developed by data users to specify the quality of data needed from a particular data collection activity (USEPA Draft, 1984).

DQO development is an iterative process involving both decision makers and technical staff. DQOs, which are statements of the quality of data needed to support a specific decision or action, are developed in three general stages. First, the decision maker and the technical staff discuss the problem being addressed, the resource and time constaints for addressing the problem, and the information needed. Second, the decision maker and the technical staff discuss specific questions developed by the staff to clarify what information is needed, how the information will be used, and what limitations of the information will be acceptable. Third, the technical staff develops possible approaches for collecting the necessary data and determines the quality of the data that can be expected from each approach. The outcome of the third stage is the decision maker's selection of the specific approach that will be used and the statement of the DQOs for that approach.

The quality of a data set is represented in terms of five characteristics of the data: precision, accuracy, representativeness, completeness, and comparability.

The objectives of a study or monitoring program should include the following concepts:

- What information is needed and what function the information serves in addressing the problem;
- How the information will be used, in terms of the types of conclusions that are anticipated from the data and the criteria that will be used to make decisions;
- The limitations and applicability of the data, in terms of the universe to which the conclusions and decisions will apply;
- How conclusions based on the data can be in error and what level of risk of making incorrect or questionable decisions is acceptable;
- The time and resource constraints for data collection.

The study or monitoring objectives are the input for stage three of the DQO development process.

DQOs are the important starting point for the detailed design of a data collection effort and are the basis for specifying the quality assurance and quality control activities associated with the data collection process. QA Project Plans are required of all USEPA data collection activities. Such plans clearly describe what will be done at each stage of data collection (i.e., sample site selection, sample collection, handling and analysis, and data handling and analysis) and include instructions or standard operating procedures for each field and laboratory activity.

During the detailed planning and preparation of technical guidance for data collectors, DQOs are used as the starting point for developing explicit, quantitative statements of the type of errors that will be controlled, the level to which these errors will be controlled, and the information that will be collected in order to characterize all the known sources of error. These quantitative statements are known as data quality indicators. Data quality indicators are needed in order to select appropriate methods for sample collection, laboratory analysis and statistical data analysis. They are also the basis for selecting QA and QC procedures (USEPA Draft, 1984).

In the remainder of this report the general guidance provided above will be applied to selected aspects of sediment sampling programs. The cogent relationship among the objectives for sediment sampling, the DQOs, and the QA/QC plan should constantly be kept in mind.

In Chapter 1 some possible objectives of sediment sampling were identified as:

- Determining the extent to which sediments act as either sources or sinks for water pollutants,
- Determining presence and distribution of selected pollutants in sediments in both space and time,
- Determining the risk to human health and/or the environment from sediment contamination by selected pollutants, and
- Taking measurements for validation of sediment transport and deposition models.

Each of these objectives will now be examined identifying possible actions which might be taken once the objectives have been achieved.

In essence, the mission of the USEPA is to control environmental pollutants and to abate potential adverse effects on man and/or the environment. Complying with this mission requires identifying significant sources of pollutants of concern, and linking these source emissions via exposure of important receptors to adverse effects. Thus, to carry out the intent of, for example, the Clean Water Act, concentrations of hazardous pollutants in waters should not be allowed to exceed levels established as being adequately protective of man and the environment when the intended uses of the waters are taken into consideration. Identification of the sources of the pollutant of concern should not only include the present emissions but also an assessment of likely future emissions. For example, one needs to establish the role of sediments as sources or sinks for selected water pollutants and how that role may change in time and space, and also the effect of such physical parameters as water temperature, depth, pH, and flow rates, suspended solids, bedload, and geological factors on that role. Biological factors may also be involved in the degradation or transformation of pollutants into different substances.

If, for example, significant quantities of the pollutants of concern become essentially permanently attached to the sediments and remain biologically unavailable, the sediments may constitute a sink for the selected pollutants. Control needs for these selected pollutants may be reduced by the amounts which the sediments remove in the sense described above, provided that no harm from the added load of pollutants comes to the biota dwelling in the sediments. Underestimates of the ability of sediments to act as a sink might lead to source control requirements more stringent than necessary, whereas overestimates might lead to less stringent control requirements than necessary.

However, one should use sediments as a sink for contaminants with caution. When the sediments become contaminated, dredging as a clean up measure is a complicated proposition. It involves extensive testing of the sediment and proposed disposal options to determine which one will have the least environmental impact. With a badly contaminated sediment one ends up with the problem of what to do with the material once it has been dredged.

If significant quantities of the selected pollutants are found to be associated with sediments initially and then released slowly over relatively long periods of time, the sediments in essence act as a pollutant source. In this instance, to keep concentrations of the pollutants below acceptable levels in downstream waters, it may be necessary to either over-control industrial, municipal, or non-point sources, or remove some or all of the polluted sediments by dredging. Underestimation of the extent to which sediments act as sources might lead to insufficient controls of other sources, whereas overestimation might lead to controls more stringent than necessary and perhaps even to the institution of expensive dredging operations to a greater degree than necessary.

The determination of the presence and distribution of selected pollutants in sediments in both space and time is necessary to achieve source or sink monitoring objectives. One possible action which might be taken on the basis of the mere presence of selected pollutants without regard to whether the sediments act as a source or as a sink is related to a case covered under the hazardous wastes regulations (CERCLA or RCRA). If the selected pollutants are constituents being stored, treated, or disposed of at a permitted hazardous waste facility, and there is probable cause that they have originated from this facility, there may be grounds for revoking the permit of the facility. Reporting the pollutants present in the sediments when they are not there would be a Type I error and might lead to the revoking of a hazardous waste facility permit when the facility is not in violation. Failing to report the pollutants present in the sediments when they are there would be a Type II error and would lead to allowing a hazardous waste facility to continue operations when it is in violation of its permit.

Determination of risk to human health and the environment from contaminated sediments involves several steps. What is ultimately required are exposure distributions to the most sensitive population of receptors of concern via all significant exposure pathways involving sediments. This will involve concern over possible exposure to water in contact with the sediments either through ingestion or skin absorption, as well as concern over possible exposure through ingestion of food contaminated directly or indirectly through contact with sediments (crops or domestic animals using water which has been in contact with the sediments, and/or aquatic foods such as fish or shellfish contaminated directly or indirectly from the sediments). It is generally the water in contact with the sediments which leads ultimately to the exposure of receptors. Thus, it is important to measure or estimate the extent to which the sediments act as a source (to contacting waters) for the pollutant(s) of concern. Knowing the concentration of pollutants in water originating from contaminated sediments is not sufficient for estimating exposure. An additional parameter required is the biological availability of the pollutant(s) of concern. For example, if pollutants are not incorporated into the edible parts of seafood, even large concentrations in the water might not lead to significant human exposure through ingestion of aquatic food stuffs.

Once desired exposure distributions have been constructed, comparison to established exposure-response relationships enables a determination of whether or not the existing risk is acceptable. Underestimation of the exposures might lead to accepting an unacceptable risk, whereas overestimation of the exposures might lead to unnecessary, and possibly costly, control actions.

The taking of measurements for validation of sediment transport and deposition models will not normally lead to control actions. Thus, positive or negative errors are unlikely to lead to corresponding over or under estimates of control needs. However, errors of unknown direction and size, if sufficiently large, might seem to validate an erroneous model or fail to validate an acceptable model. The consequences of such errors cannot be evaluated without knowing the purposes for which the model might be used and what actions might be taken on the basis of conclusions drawn from the model.

The point to be made is that, prior to undertaking any sediment sampling program to achieve defined objectives, it is necessary to establish acceptable levels of precision for end results. These should be established after due consideration of the consequences of taking actions which might subsequently be shown not to be justified on the basis of the available data.

Once levels of precision have been established, an experimental protocol should be prepared setting forth what is to be done for what purpose; and how, when, where and how many samples will be collected. Also, the protocol should indicate how the samples will be prepared for analysis and then analyzed for what substances, and how the resulting data will be validated, analyzed and interpreted. As part of this protocol, a complete QA/QC plan must be included covering all aspects of the experimental program with special attention to sampling aspects. In the remainder of this report, additional details will be presented with regard to specific required elements of the QA/QC plan for various kinds of sediment sampling programs.

GENERAL IDENTIFICATION OF THE OBJECTIVES

Some functional objectives for sediment sampling and associated QA/QC programs have been identified and discussed. This material will now be recast for application to problems related to carrying out the provisions and intent of RCRA and

CERCLA. Operational situations in which sediment sampling may be involved include:

- Preliminary site investigations
- Emergency cleanup operations
- Planned removal operations
- Remedial response operations
- Monitoring
- Research or technology transfer studies

With the possible exception of research or technology transfer studies, all of the operational situations listed have a potential for litigation. For this reason, a statistical experimental design incorporating appropriate QA/QC measures including "chain-of-custody" procedures should be incorporated into the sampling program. The total QA/QC plan should require that the accuracy and comparability of the analytical methods used, as well as the precision and representativeness of the sampling, be demonstrated. Generally, the demonstration of accuracy and comparability will be part of the QA/QC plan for the appropriate analytical laboratory. Demonstration of the precision and representativeness of the sampling must be part of the QA/QC plan incorporated into the sampling protocol. Precision measures the repeatability of the results obtained from analyzing the collected sediment samples. Representativeness of the sample has two components: the sample taken must reflect what is actually present in the sediment (this is difficult to quantify) and, the reliability of the mean and standard deviation as measures of the amount of a chemical present in a particular area must be established. Increased sampling intensity, independent sampling, and sampling audits are examples of techniques that help ensure that the sample is representative of the condition in the area under investigation.

The purpose of a preliminary site investigation is to provide information about a specific site that can be used in making initial management decisions, and, should further work be necessary, for designing a more detailed and comprehensive sampling investigation. Since the data collected during the preliminary study will be used to make important decisions about the site, it is essential that the reliability of the data be demonstrated through incorporation and implementation of an adequate QA/QC plan for this investigation. For example, the preliminary results may indicate that an emergency response should be initiated. Making an erroneous decision based upon data of unknown quality concerning such an important matter could lead to serious consequences.

The purpose of an emergency cleanup operation is to remove enough of the pollutants as quickly as possible to achieve a level that is not considered an unacceptable threat to human health or the environment. The principal role of the QA/QC plan in this situation is to provide a reliable demonstration that cleanup operations have been adequate. An emergency cleanup operation often leads to a requirement for either a planned removal or a remedial response operation. Thus, any sediment sampling undertaken during the emergency phase should have adequate QA/QC measures to ensure that the resulting data may be used as a foundation for any subsequent investigations.

The purpose of planned removal or remedial response operations (they differ principally with regard to time scale) is to provide a more permanent solution to the problem. These operations may involve extensive sampling and data analysis programs. Adequate QA/QC measures are essential since litigation to recover the costs of the operations is a likely sequel. Consequently, all data collected may well undergo close scrutiny in court.

Monitoring, or sequential measurements over time, may take place before, during, or after any of the operational situations listed above. Whatever trends are measured must be demonstrated to be reliable in order to serve as a basis for making decisions that hold up to challenges.

The purposes of research or technology transfer studies vary widely. In any event, the incorporation of adequate QA/QC plans into these studies is mandatory in order for the results of the studies to withstand the normal peer review processes required for publication and/or application of the findings.

In summmary, an adequate QA/QC plan should be part of any sediment sampling program relevant to any of the operational situations listed. The only question remaining pertains to the definition of the word "adequate." That question will be addressed in a subsequent section of this chapter.

OBJECTIVES FOR BACKGROUND MONITORING

Generally the design of sediment monitoring programs requires that the levels of defined hazardous or potentially hazardous substances and their spatial and temporal trends be measured for some specific purpose. Often it is critical not only to quantify levels and trends but also to link the existing levels to sources. This is necessary to enable adequate control actions to be taken whenever a situation that is hazardous to human health, welfare, or the environment is identified. Often the situation is complicated by the fact that multiple sources contribute to the measured levels.

The situation is further complicated by the presence of pollutants of recent origin mixed with pollutants of past origin. This mixing becomes especially important when the investigator attempts to trace the migration from source to receptor and also in predicting what future levels are likely to be after various proposed control measures are implemented.

Identification of spatial and temporal trends along with linkage of observed measurements to sources requires that adequate background or reference or control samples be taken.

In the absence of such background samples, interpretation of the resulting data may become extremely difficult, if not impossible. The burden of proof that background samples are not necessary for a particular sediment monitoring study rests with the principal investigator. In the absence of such proof, a prudent investigator will ensure that the collection of adequate background samples is included in the monitoring study design. Furthermore, some EPA regulations concerning regulatory monitoring (U. S. Code of Federal Regulations, 1983) specifically require background sampling.

Since measured levels in presumably higher concentration areas will be compared to background levels, QA/QC procedures are just as critical for the background measurements as they are for the study area measurements. Thus, for background sampling, a QA/QC procedural umbrella must cover the selection of appropriate geographical areas, the selection of sampling sites within the geographical areas, sampling, sample storage and/or preparation, sample analysis, data reduction, and interpretation of study results.

Under most circumstances, background data will not be available for a given monitoring location. These data must be acquired either before or during the exploratory or preliminary investigation phase. The intensity of the background sampling that is undertaken depends upon the pollutants being measured, the sediment characteristics and variability, the levels of pollutant likely to be found in the study area and the purpose of the study.

SPECIFIC OBJECTIVES FOR MONITORING IN SUPPORT OF CERCLA

The principal sampling media now being measured to carry out the provisions and intent of CERCLA, and RCRA as well, are soil and groundwater. What, then, is the proper role for sediment sampling in support of CERCLA? Hazardous constituents from a hazardous waste facility may enter sediments through transport of the constituents from the waste site to sediment, via either surface water or groundwater flow into receiving bodies of water. Air transport followed by rainout or washout will generally be less important than the other two transport routes. What information can be gained, then, from sediment measurements which cannot be gained from soil, air, surface water, or groundwater measurements?

Suppose a situation exists in which hazardous waste constituents have been leaving a site for a relatively long period of time and an adjacent body of water has built up a considerable amount of selected constituents in its sediments. Further, suppose that the sediments now constitute a source of the hazardous constituents. At this time, removal of the hazardous wastes from their original disposal site may still leave an unsolved significant problem in the form of the contaminated sediments. Human foods, contaminated directly or indirectly through contact with sediments, may be unfit for human consumption. Furthermore, as the hazardous constituents move through different trophic levels, substantial biomagnification of contaminants may take place, thereby increasing the risk to humans consuming foods from higher trophic levels. Thus, it is conceivable that situations may exist in which concentrations of hazardous constituents in sediments may represent a major risk to human health or the environment. To identify such situations, data from sediment sampling is an important link in the chain of required evidence

The steps outlined below are designed to provide a sediment monitoring effort with adequate sample precision and representativeness (USEPA, FR44:233, 1979 and Bauer, 1971).

1. Identify the objectives of the study.

2. Determine the components of variance that should be built into the statistical design.

3. Choose the allowable probabilities for Type I and Type II errors and the difference in means considered to be significant. (These choices together with an estimate of the coefficient of variation are needed to determine the number of samples required in each stratified region.)

4. Obtain sampling data from other studies with similar characteristics to the one of interest. (Estimates of coefficients of variation are of particular importance.)

5. Calculate the mean and note the range of each set of duplicates (co-located independent samples).

6. Group the sets of duplicates according to concentration ranges and by the types of samples believed to be similar.

7. Calculate the critical difference R_C (number not to be exceeded to maintain adequate QA/QC) from the formula

$$R_C = \frac{3.27\ C}{n} \sum_{i=1}^{n} \frac{R_i}{\bar{X}_i}$$

where C = concentration, n = number of duplicate analyses, R_i = range = x_i ⁻)(x_{i+1} ,
and $\bar{X}_i$ = mean = $(x_i + x_{i+1})/2$.

8. Using results from previous studies, develop a table of R_C values for various concentrations that span the range of concentrations of interest. (These data are used to accept or reject sets of duplicate samples.)

9. Use the preliminary R_C table to accept or reject sets of duplicates. When approximately 15 pairs (USEPA, 1979) of results from the present study are available, a new table of R_C values should be constructed based upon the data that have been accepted.

10. Use data collected during the preliminary or exploratory site investigation and any emergency response activity as the data base upon which later studies are evaluated and/or designed.

Suggestions for additional elements of a more complete QA/QC plan are provided in subsequent chapters.

The specific goals for each type of study will determine the allowable probabilities of Type I and Type II errors and the minimum relative difference between sampled population mean and either background mean, or designated action level that is considered important to detect. Suggested guidelines are given below for the operational situations listed previously.

PRELIMINARY SITE INVESTIGATION

The preliminary or exploratory investigation is the foundation upon which other studies in hazardous waste site assessments should be based. As part of this study, it is essential to determine whether or not sediments are sample media of importance to the total assessment. The total assessment must draw conclusions with regard to whether or not there is imminent and substantial danger to human health requiring emergency action and whether there is an unacceptable long term risk to man or the environment. If sediments are determined to be unimportant in the preliminary study, it is likely that no further attention will be directed to them. In view of this, a Type II error is considered to be of greater importance than a Type I error. Presented below are suggested guidelines for DQOs that may be used initially.

Confidence Level $(1 - \alpha)$	Power $(1 - \beta)$	Relative Increase over Background $[100(\mu_S-\mu_B)/\mu_B]$ to be Detectable with a Probability $(1-\beta)$
70-80%	90-95%	10-20%

If resources limit the number of samples that can be taken, the investigator should determine, for the number of samples that can be collected, value-judgment based optimum values for confidence level, power, and detectable relative difference. If these values are deemed adequate, the study may proceed.

Using five percent duplicate samples may provide adequate QA/QC for measuring variance between samples (Plumb, 1981). However, there should be a minimum of two sets of duplicates in each strata sampled. As data become available, these assumptions should be checked. This is usually accomplished by taking and analyzing more duplicates initially, and then checking to determine the minimum number required for the sites being sampled and the pollutants being measured.

EMERGENCY CLEANUP

Emergency sampling is designed to identify those areas in which sediments are contaminated to such a degree as to threaten imminent and substantial endangerment to human health. The threat may be due to the sediments acting as a source of hazardous constituents to drinking water or to human foods. The emergency action in either event is more apt to be switching to bottled water for drinking and/or taking certain locally produced human foods off the market than it is to be a dredging program to remove the contaminated sediments. Dredging may well be implemented at a later date as part of a planned removal or a remedial response operation. Of course, any long term solution to the problem would also have to address the removal of the primary source of hazardous substances to the sediments.

For an emergency response operation involving sediments, a Type II error is considered of greater importance than a Type I error. Presented below are suggested guidelines for DQOs that may be used for emergency response operations.

Confidence Level $(1 - \alpha)$	Power $(1 - \beta)$	Relative Increase from Background or an Action Level to be Detectable with Probability $(1-\beta)$
80-90%	90 - 95%	10 - 20%

PLANNED REMOVAL AND REMEDIAL RESPONSE STUDIES

These studies are usually continuations of those initiated during emergency cleanup studies. They should be designed to provide specific information needed to resolve control option issues. The areas to be surveyed should be stratified and sampled according to a design that can be used to determine spatial variability. A suitable statistical design should be formulated so that components of variance for the study situation may be identified and evaluated. Appropriate QA/QC procedures must be formulated and implemented.

If the sampling during exploratory or emergency response investigations has been done properly, there will be a sound basis for determining the sample size and sampling site distributions. The design will have to incorporate information on the vertical distribution as well as the horizontal distributions. Measurements of concentration trends with time may be of critical importance particularly if sediment concentrations are changing appreciably with time. For example, sediments may at least partially cleanse themselves once the primary source of contamination is removed. This cleansing process, or reduction in concentration of contaminants in sediments, may be due to a combination of biotic degradation of the contaminants together with the addition of uncontaminated sediments.

For a planned removal or a remedial response operation involving sediments, it is considered that a Type I and a Type II error are of about equal significance. Furthermore, an attempt at cost recovery which might lead to mitigation is a likely successor to these studies. Accordingly, it is important to achieve the highest order of precision feasible. Presented below are suggested guidelines for DQOs that may be used for planned removal and remedial response studies.

Confidence Level $(1 - \alpha)$	Power $(1 - \beta)$	Relative Increase from Background or an Action Level to Be Detectable with Probability $(1-\beta)$
90-95%	90-95%	10-20%

MONITORING OR RESEARCH STUDIES

The guidelines for these studies for confidence levels, power, and detectable relative differences should be set on the basis of the objectives of the studies. As actions which may be taken on the basis of resulting data become more and more significant and costly, greater effort should be placed on achieving an increased level of reliability for the data. Publication of the results in a peer-reviewed journal will also usually require some demonstration that an adequate QA/QC plan has been incorporated into the experimental protocol.

CHAPTER 4

STATISTICAL CONSIDERATIONS

INTRODUCTION

This chapter reviews the role of statistics in the sediment pollution monitoring process. Statistics is a science of data collection and analysis to efficiently obtain information concerning questions of interest. Without statistics there would be no basis for comparison of sampling procedures of equal cost. There are numerous texts and journals dealing with statistics. Some references that relate to the statistics of sediment sampling are given in this chapter. The techniques presented in these references will not be discussed in detail. The user is encouraged to utilize the referenced materials if additional information is required. However, in the actual planning of a sediment sampling design the reader is advised to consult a professional statistician.

DISTRIBUTION OF SEDIMENT SAMPLING DATA

Statistical sampling plans are based on assumptions concerning the probability distributions of the measurements to be made. These assumptions should be consistent with results from past surveys taken under similar conditions. The variability in sample data is a function of the variable being measured, the analytical procedure, and the sampling procedure. If the distribution of a measurement is normal, it is symmetric about its expected value (center of gravity of the probability distribution) and its variability is uniquely determined by its variance (variance is the moment of inertia of the probability distribution about its mean when probability is treated as mass). The symmetry makes the expected value a reasonable measure of location, whereas in non-symmetric distributions other measures may be preferred (e.g., the median). Also, the statistician has means of dividing variance into components representing various sources of variation. With most other probability distributions, the variability is only partially described by the variance. Hence, these properties of symmetry, and variance representing variation, are two of the prime reasons for transforming variables so that the new distributions are approximately normal. Procedures for such transformations are given in Box and Cox (1964) and in Hoaglin et al. (1983). A discussion of the importance of the normality assumption and some possible transformations appears in Scheffe (1959, Chapter 10). In what follows, we shall assume that the data have been transformed to near normality.

In the paragraph above, only variables with quantitative measurements were considered. If the variable of interest has a count measurement, such as radioactivity or presence or absence of a pollutant, other statistical methods are required. These methods are usually denoted qualitative or discrete statistical methods. Bishop et al. (1975) is a good reference to these procedures. The methods of this chapter should not be applied to count data.

The environmental scientist can obtain information on the distribution of a variable by conducting an exploratory or pilot study. The exploratory studies conducted during the initial phases of an investigation can provide an indication of the site specific probability distribution pattern and the transformation to normality that may be needed. McKay and Paterson (1984) discuss the use of the normal, log normal and Weibull distribtions in environmental studies. The environmental scientist is interested in finding the location and amounts of pollutants that emanated from a source;

therefore the pilot study should provide information on both contaminated and background sediment areas.

Additional information about the distributions of measurements of pollutants may be obtained from EPA's Regional Offices and Laboratories and EPA's National Enforcement Investigation Center in Denver, Colorado.

STATISTICAL DESIGNS

The design and method of analysis for the sampling study must be determined before the sampling is undertaken. Improper design or analysis may invalidate the resulting conclusions, or prevent valid conclusions from being made. Care must be taken not to allow time of sampling to be confounded with an effect being estimated. Also it is very important that the individual samples and subsamples be taken in such a way that the measurements are comparable. Basic ideas of sampling design may be found in Hansen et al. (1953) and Gy (1982). Two of the simpler designs are the simple random sampling design and the stratified random design. In the simple random sampling design, the n sample points are randomly selected in such a way that all combinations of n points in the population have the same chance of being chosen. While the simple random design allows easy methods for the analysis of data, it is inefficient in the use of resources and is infrequently used in practice. The stratified random design is one in which the area under study is subdivided into smaller areas (strata) that have the potential of being markedly different in pollutant concentrations and then simple random sampling is done within each stratum. This procedure ensures that no large sub-area is without sample points and thereby helps reduce sampling variance when there are substantial differences in concentrations between strata. Methods for optimizing the choice of the number of strata and number of points within strata are given in the text by Hansen et al.(1953).

There are two basic approaches to the planning and analysis of sediment sampling. One is the traditional sampling model approach, found in Hansen et al.(1953), which uses randomization in the selection of sample points, as a probability basis for statistical inference, and an analysis-of-variance model approach to inference. The second is a "geostatistical" model approach using the idea that an underlying random process created the spatial distribution of the variable. The geostatistical approach involves the estimation of spatial structure of random functions and kriging to estimate isopleths of variable values. An introduction to these procedures may be found in Journel and Huijbregts (1978). The methods given in this chapter relate to the more traditional analysis-of-variance sampling model.

Type I and Type II Errors

The environmental manager may wish to make an informed decision through a statistical test of hypothesis based on the sediment samples. For example, he may need to decide whether the study area is contaminated or not. The hypothesis to be tested is the "null" hypothesis of no contamination, which might be expressed as

$$H: \mu_S = \mu_B \text{ (or } \mu_S \leq \mu_B)$$

where μ stands for the mean of a population and the subscripts S and B stand for the study and background populations respectively. If the test rejects the hypothesis above, then the alternative hypothesis of study-area contamination

$$A: \mu_S > \mu_B$$

is accepted. This test is a one-sided test in that A is $\mu_S > \mu_B$. In a two-sided test, the two hypotheses are $H: \mu_S \neq \mu_B$, and

A: $_S=\ _B$. For example, the two-sided test may be of interest in determining whether pollutants have caused a change in pH.

A test of hypothesis is basically a decision rule specifying a test statistic (i.e., a function of the sample data) and a set of possible values of that test statistic, called the critical region of the test, such that if the value of the test statistic for the obtained sample data is in the critical region, the null hypothesis is rejected and the alternative hypothesis is accepted. If the value of the test statistic does not fall in the critical region, the alternative hypothesis is not accepted. Two types of error are possible. The acceptance of the alternative hypothesis when the null hypothesis is true (false positive) is said to be a Type I error. Failure to accept the alternative hypothesis when it is true (false negative) is a Type II error. The two types of error may be equally well defined in terms of acceptance and rejection of the null hypothesis. Then one would say that if the value of the test statistic is in the critical region, the conclusion is to reject the null hypothesis; otherwise one accepts the null hypothesis. Similarly, one may call the complement of the critical region, the acceptance region. Figure 4 illustrates a two-sided test situation where the acceptance region is the interval below the center of the density curve and the critical region consists of the two intervals below shaded tails of the density curve. The maximum probability allowed for a Type I error in testing a hypothesis is called the significance level of the test. The significance level of a test is commonly denoted by the Greek letter alpha (α), Typical values used for significance levels are 0.001, 0.01, 0.05 and 0.10. The value chosen depends on the consequences of making a Type I error and is not limited to the typical values. The diagram below illustrates the relationships described for Type I and Type II errors.

		TRUTH	
		H	A
DECISION:	Accept H	Correct	Type II Error
	Accept A	Type I Error	Correct

The probability of a Type II error (i.e., the probability of accepting the null hypothesis when it is false) is usually denoted by the Greek letter beta (β) and is typically a function of α, sample size, and the size of the deviation from the null hypothesis. The probability that the alternative hypothesis will be accepted when it is true (i.e., the probability that the test statistic will take on a value in the critical region when the alternative hypothesis is true) is called the power of the test and may be denoted by $(1-\beta)$. Typically, the experimenter will specify the smallest deviation from the null hypothesis that he considers to be scientifically, economically, or environmentally important to detect and then specify the power of the test that he wants for that specific alternative. Obviously he wants the test to have high power for the scientifically important alternative and low significance level. However, it is evident that if one increases power by increasing the size of the critical region, one is also increasing significance level. One way to increase power, without increasing significance level is to increase the amount of information; that is, increase the sample size.

Figure 4b shows the probability density curve for a test statistic under the null hypothesis,

$$H: \mu = 30.0$$

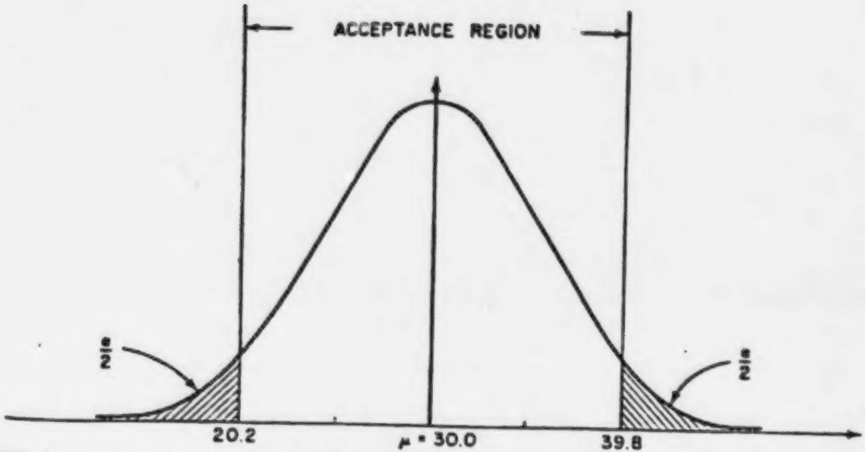
ACCEPTANCE REGION
$\frac{\alpha}{2}$
$\frac{\alpha}{2}$
20.2
$\mu = 30.0$
39.8

Fig. 4a Acceptance region for $H: \mu_0 = 30.0$.

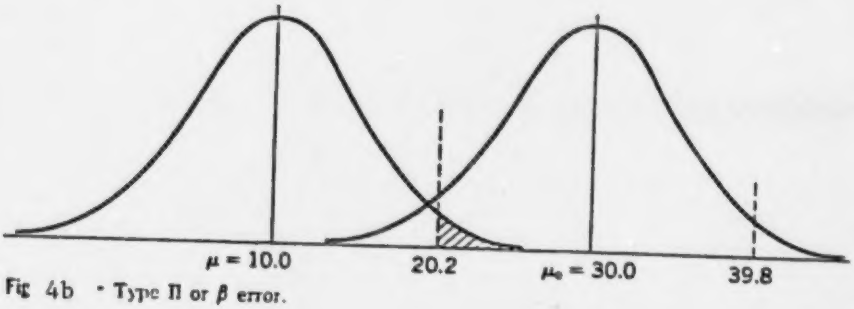
$\mu = 10.0$
20.2
$\mu_0 = 30.0$
39.8

Fig 4b - Type II or β error.

The shaded portion represents the probability of a Type I error (α). In Figure 4b the left curve represents the probability density function of the test statistic when $\mu = 10$. The shaded area in Figure 4b represents the probability (β) of a Type II error in this situation (Juran et al., 1979).

Number and Location of Samples

There are three basic procedures for increasing the precision of statistical estimators and the power of statistical tests. They are (i) use more efficient statistical estimators and tests, (ii) improve the sampling design, and (iii) increase the sample sizes. Table 11 in Chapter 6 gives information on sample sizes to use when employing t-tests of means. Discussion concerning the origin and use of these tables is also given in Chapter 6. Additional tables for the determination of sample sizes can be found in Beyer (1968). The use of t-tests requires some form of random selection process so that the standard deviation of an observation may be estimated.

Stratification is a sampling procedure for improving precision of estimates. This technique makes use of scientific knowledge that the measurements may be quite different in different identifiable segments of the area being sampled. A typical stratification criterion used in soil science is the soil type. Another criterion that might be useful in sediment sampling is distance from point sources of pollutants.

Role of Quality Assurance in Experimental Design

The Quality Assurance Officer should be intimately involved in the review of the experimental or sampling design proposed by the investigator. He should require that the information obtained provide measures of the components of variance that are identified in the field. An additional quality check that should be undertaken as part of the QA program is the review of the design by qualified sediment scientists and other peers that are in a position to provide the necessary oversight of the sampling effort.

Broms (1980) makes the following statement; "There should be a balance between the soil investigation method, the quality of the soil samples, and the care and skill spent on the preparation and the testing of the samples. There is no point in spending time and money on careful sample preparation and on testing if the quality of the samples is poor." This statement is equally applicable to sediment sampling. The QA program must address the total flow of information from the design to the reporting of the results. The sampling design is the foundation of the whole study, therefore, it should be given maximum support if the purposes of the sampling effort are to be met.

Components of Variance

The components of variance analysis, (see Scheffe, Chapters 7 and 8) provides estimates of the portion of the total variation coming from each of the sources of variation in the measurements. Basic assumptions of this procedure are that the measurements are normal in distribution, independent, and each source has constant variance. An excellent example of the use of this technique is provided in a report by the Electric Power Research Institute (Eynon and Switzer, 1983). An example presented in Table 3 gives the components of variance for hypothetical sample data from a stratified random design with four strata, three random samples per stratum, two subsamples per sample, and one analysis per subsample. (The stratum effects are assumed fixed here, so this is really a mixed-model

TABLE 3. ANALYSIS OF VARIANCE OF A NESTED SEDIMENT SAMPLING DESIGN.

Stratum (i)	Sample (j)	Subsample (k)	X_{ijk}	X_{ij}	$X_{i..}$	$X_{...}$
1	1	1	3.17			
		2	2.64	5.81		
	2	1	1.79			
		2	3.00	4.79		
	3	1	2.20			
		2	1.95	4.15	14.75	
2	1	1	1.10			
		2	2.94	4.04		
	2	1	2.77			
		2	1.95	4.72		
	3	1	2.71			
		2	3.00	5.71	14.47	
3	1	1	4.33			
		2	4.50	8.83		
	2	1	4.25			
		2	4.53	8.78		
	3	1	3.87			
		2	4.79	8.66	26.27	
4	1	1	5.03			
		2	4.65	9.68		
	2	1	3.95			
		2	3.76	7.71		
	3	1	4.79			
		2	4.63	9.42	26.81	82.30
a=4	b=3	n=2				

I. $C = (X_{...})^2/(abn) = (82.30)^2/24 = 282.2204$

II. Total: $\Sigma X^2_{ijk} - C = (3.17^2+...+4.63^2) - 282.2204 = 29.8656$

III. Strata: $\Sigma X_{i..}^2/bn - C = (14.75^2+...+26.81^2)/6 - C = 23.7517$

IV. Samples: $\Sigma X^2_{ij}/n - C = (5.81^2+...+9.42^2)/2 - C = 26.3109$

V. Samples in Strata: IV - III = 2.5592

VI. Analysis of Sample: II - IV = 3.5547

ANOVA TABLE

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square	Expected Mean Square
Strata	3	23.7517	7.9172	$V_A + nV_S + bnM/3$
Samples/Strata	8	2.5592	0.3199	$V_A + nV_S$
Analysis/Samples/ Strata (error)	12	3.557	0.2962	V_A
Total	23	29.8656		

$s^2 = 0.2962$ estimates V_A or variance due to subsampling and analysis

$s^2 = (0.3199 - 0.2962)/2 = 0.0118$ estimates V_S

where V_S is the variance due to sampling within strata.

M = Sum of squared deviations of stratum means about grand mean.

analysis (i.e., some random and some fixed effects), but it does provide estimates of components of variance from within stratum sampling and combined subsampling and analytical errors). The results in Table 3 would indicate that the experimenter should either have made a greater effort to reduce subsampling and analytical errors or taken more subsamples since the error variance is much larger than the variance between samples within strata.

Compositing of Samples

A technique that is often employed to reduce sample handling and analytical costs is the compositing of samples. Combining the samples from several sampling locations reduces the costs for analysis. This procedure is used extensively by agricultural workers to determine fertilizer requirements for farm fields. Peterson and Calvin (1965) make the following statement about the technique:

> "It should be pointed out that the composite samples provide only an estimate of the mean of the population from which the samples forming the composite are drawn. No estimate of the variance of the mean, and hence, the precision with which the mean is estimated can be obtained from a composite of samples. It is not sufficient to analyze two or more subsamples from the same composite to obtain an estimate of the variation within the population. Such a procedure would permit the estimation of variation among subsamples within the composite, but not the variation among samples in the field. Similarly, if composites are formed from samples within different parts of a population, the variability among the parts, but not the variability within the parts, can be estimated. If an estimate of the variability among sampling units within the

population is required, two or more samples taken at random within the population must be analyzed separately."

Youden and Steiner (1975) caution against the use of the composite sample for much the same reasons as those outlined above. Since a prime purpose of QA/QC is to assess and assure the accuracy (i.e., lack of bias and level of precision) of the data and of estimates obtained from the data, it is essential that estimates of the precision be made from the data. Therefore, the compositing of samples cannot, in general, be recommended.

Some work on determining the precision of estimates of the mean from composite samples has been published. Such estimates of precision usually require some strong assumptions about variance components and/or the stochastic nature of the composited samples (see Duncan (1962) and Elder, et al. (1980)).

Split Samples, Spiked Samples and Blanks

Split samples, spiked samples and blanks are used to provide a measure of the internal consistency of the samples and to provide an estimate of the components of variance and the bias in the analytical process. To obtain an unbiased measure of the internal consistency of samples and their analyses, the individual samples should be labeled with a code number in such a way that the chemist (and preferably also the laboratory) do not know the relationship between the samples that he is analyzing. This reduces the chances of conscious or unconscious efforts to improve the apparent consistency of the analyses.

Samples can be split to:

- Provide samples for both parties in a litigation or potential litigation situation.

- Provide a measure of the within sample variability (this is needed in order to determine the influence of other factors that may be confounded with sample splitting.)
- Provide materials for spiking in order to test recovery.
- Provide a measure of the sample bank and extraction error.

The location of the sample splitting determines the component of variation that is measured by the split. A split made in the sample bank measures error introduced from that level onward. A split made in the field includes errors associated with field handling. A split or series of subsamples made in the laboratory for extraction purposes measures the extraction error and subsequent analytical errors.

Spiked samples are prepared by adding a known amount of reference chemical to one of a pair of split samples. The results of the analysis of a split compared with the non-spike member of the split measures the recovery of the analytical process and also provides a measure of the analytical bias.

Spike samples are difficult to prepare with sediment material itself. Frequently the spike solution is added to the extract of the sediments. This avoids the problem of mixing, etc. but does not provide a measure of the interaction of the chemicals in the sediments with the spike, nor does it provide an evaluation of the extraction efficiency.

Blanks provide a measure of various cross-contamination sources, background levels in the reagents, decontamination efficiency and any other potential error that can be introduced from sources other than the sample. For example, a trip blank measures any contamination that may be introduced into the sample during shipment of containers from the laboratory to the field and back to the laboratory. A field blank measures input from contaminated dust or air into the sample. A decontamination blank measures any chemical that may have been in the sample container or on the tools after decontamination is completed.

The number of QA/QC samples have been selected by a rule of thumb that one out of every twenty samples is to be assigned to each of the categories of samples. This ratio has been used successfully in several major USEPA studies (USEPA, 1982, 1984). Table 4 presents the breakdown of QA/QC samples used in these previously conducted monitoring studies.

DATA ANALYSIS

The topics that follow are designed to provide insight into the use of statistical techniques for evaluating the data obtained during an investigation. They are not by any means exhaustive, but are chosen to provide the basis for designing the quality assurance portions of a sampling effort and to provide the basis for obtaining the most benefit from the data acquired.

Bias

The variation seen in analytical data can be composed of variation within the sample itself, variation introduced in sample collection or preparation and variation in the analysis of the samples. The variation can further be divided into sample variation and bias. Bias identifies a systematic component of the error that causes the mean value of the sample data to be either higher or lower than the true mean value of the samples. Bias must be due to a fault in the sampling design, sampling procedure, analytical procedure or statistical sample. An example of a bias would be the error in analytical results introduced by an instrument being out of calibration during a portion of the analysis. Laboratories usually introduce reference samples into their sample load in order to detect these changes. Bias in sediment sampling is difficult to detect. The

TABLE 4. QA/QC PROCEDURES FOR SEDIMENT SAMPLES

Procedure	Comments
1. Field Blanks	One for each sampling team per day. A sample container filled with distilled, de-ionized water, exposed during sampling then analyzed to detect accidental or incidental contamination.
2. Sample Bank Blanks	The blank, about one for each 40 samples, passed through the sample preparation apparatus, after cleaning, to check for residual contamination.
3. Decontamination Blanks	A blank, about 1 for each 20 samples, passed over the sampling apparatus after cleaning, to check for residual contamination.
4. Reagent Blank	One for each 20 samples to check reagent contamination level.
5. Calibration Check Standard	One for each 20 samples to check instrument calibration.
6. Spiked Extract	One for each 20 samples to check for extract matrix effects on recovery of known added analyte.
7. Spiked Sample	One for each 20 samples. A separate aliquot of the soil sample spiked with NBS Lead Nitrate to check for soil and extract matrix effects on recovery.

TABLE 4. CONTINUED

Procedure	Comments
8. Total Recoverable	One for each 40 samples, a second aliquot of the sample is digested by a more vigorous method to check the efficacy of the protocol method.
9. Laboratory Control Standard	One for each 20 samples. A sample of NBS River Sediment carried through the analytical procedure to determine overall method bias.
10. Re-extraction	One for each 20 samples. A re-extraction of the residue from the first extraction to determine extraction efficiency.
11. Split Extract	One for each 20 samples to check injection and instrument reproducibility.
12. Triplicate Sample (Splits)	One for each 20 samples. The prepared sample is split into three portions to provide blind duplicates for the analytical laboratory and a third replicate for the referee laboratory to determine interlab precision.
13. Duplicate Sample	One for each 20 samples to determine total random error.

presence of bias can be proven by use of one of the techiques described below. On the other hand it is difficult to prove that bias is not present because the absence of bias may be the result of the inability to measure it rather than its actual absence.

Standard Additions-- It is necessary to conduct special experiments in order to detect bias in the sampling effort. The major technique used is that of adding known amounts of standard solutions to the samples: it is recommended that this be done in the field or in a field laboratory. The main problem encountered is that mixing sediments to obtain homogeneity is difficult in a laboratory much less in the field. Several known quantities of the standard are added to samples taken in the field. The results should follow the equation for a straight line:

$$y = a + b_1x$$

where x is the increase in concentration and y is the value obtained by the laboratory. Bias is indicated if the data do not follow the straight line equation, or if $a < 0$. If the units of x and y are the same, the value of b, should be unity; and significant deviations from unity indicate a proportional bias (Allmaras, 1965).

Internal Consistency-- If several samples of sediments of different size are analyzed for a constituent, the results should fit a linear equation of the form:

$$y = a + b_2Z$$

where Z is the quantity of sample analyzed. The amount of chemical detected should be directly related to the quantity of the sample analyzed. The plot of the (y,Z) data should be essentially linear; if not, bias is indicated. The intercept, a, should be within sampling error of zero and the slope b should represent the concentration of the chemical in the sediments. A linear graph in which the intercept is definitely nonzero would indicate an additive bias in the analytical procedure.

Confidence and Prediction Limits

Typically one wishes to estimate the concentration of measured pollutants in the sediments and to indicate the precision of these estimates. To indicate precision of an estimate one may provide the standard error or a confidence interval for the expected value of the concentration. Where statistical designs have been used in the sampling, the analysis of variance (ANOVA) provides needed information for calculating standard errors and confidence intervals.

The confidence interval is bounded by confidence limits (CL). The confidence limits are "the bounds of uncertainty about the average caused by the variability of the experiment" (Bauer, 1971). The limits for the mean are defined by the following equation.

$$CL = \bar{x} \pm ts/\sqrt{m}$$

where x = sample mean, s = sample standard deviation, m = number of samples and t = Student's t value at the desired level of confidence and with degrees of freedom associated with s in the ANOVA (see Appendix A, for values of t).

Consider again the example of Table 3. If all the strata represent equal area subdivisions of the study area, the logical estimate of the expected concentration for the study area is just the sample mean of the 24 measurements,

$$\bar{x} = 82.3/24 = 3.43$$

which could also be obtained by first finding the average of each pair of subsamples and then averaging these 12 sample values. The variance of the average over a pair of subsamples is

$$V_A/2.$$

When one averages over the 12 samples, a new source of variation enters in; namely, the samples-within-strata (samples/strata) variance. Therefore, the variance of the sample mean is

$$[V_S + V_A/2]/12 = (V_A + 2V_S)/24$$

The quantity,

$$V_A + 2V_S$$

is estimated by the mean square for samples/strata in the ANOVA table with 8 degrees of freedom. Therefore our estimate of the standard error of the mean, $s/\sqrt{m}$, ($s = \sqrt{0.3199} = 0.5656$ and $m = (2)(12) = 24$) is

$$0.5656/\sqrt{24} = 0.115$$

The table in Appendix A gives $t = 2.306$ for a two-sided confidence interval with 95% confidence based on an estimate of s with 8 degrees of freedom. Hence the 95% confidence interval in this case is bounded by the confidence limits.

$$CL = 3.43 \pm (2.306)(0.115) = 3.16,\ 3.70.$$

Prediction limits (PL) (see Hahn, 1969; and Guttman et al., 1982) are similar to confidence limits in appearance but are used to identify an interval into which a randomly chosen future sample value from stratum i should fall. The defining equation for these limits is:

$$PL = \bar{x}_i \pm ts\sqrt{((1/n)+(1/bn))}$$

where x_i is the sample mean for stratum i. Hence, one can say for the above example that if one more sample were randomly taken from the stratum 1, one would be 95% confident that the means of the analyses on the two subsamples would give a value between the prediction limits,

$$\begin{aligned} PL &= 2.46 \pm (2.306)(0.5656)\sqrt{((1/2)+(1/6))} \\ &= 2.46 \pm 1.06 \\ &= 1.40,\ 3.52 \end{aligned}$$

Outliers

A problem that is particularly prevalent in data obtained from field samples is that of outliers (i.e., observations that are discordant with the rest of the data set). The basic question is whether it is reasonable to expect such a discordant observation in the sample; if not, the measurement is considered an outlier. The cause of the outlier may be an error of procedure in sampling, subsampling, chemical analysis, or the transcribing of data; or it may be due to an anomaly that would indicate that a change is required in the assumed model for the process (e.g., vegetation that takes up a heavy metal being measured is not present at one of the sample points and this causes a much higher measurement at that point than at the others).

The discordance of an observation depends on the assumed probability distribution for the variable being measured. A measurement that is large relative to the other measurements may appear discordant to an observer who assumes a normal distribution for the variable, but not discordant to another observer who assumes that the probability distribution of the variable is highly skewed to the right. Hence, tests of hypotheses concerning the presence or absence of outliers are based on assumptions concerning the underlying probability distribution. Many tests have been devised for normal, gamma, and Poisson distributions. A book by Barnett and Lewis (1978) lists many of these outlier tests and also gives tables of critical values for the tests.

In environmental monitoring, extremely large measurements of pollutant concentrations are particularly disturbing. A test that is good for checking a discordant measurement on the right of a data set (i.e., the largest measurement) having an underlying normal probability distribution uses the test statistic

$$W = (Y_{(n)}-\overline{Y})/S$$

where $Y_{(n)}$ is the largest observation in a simple random sample of size n, $\overline{Y}$ is the usual sample mean, and S is the sample standard deviation. The test declares the largest observation to be an outlier if the test statistic is at least as large as the critical value for the test. Table VIIa in the book by Barnett and Lewis gives critical values for this test. For a stratified random sample, n would represent the stratum sample size and the mean would be for the stratum.

Unfortunately, there are many problems with outlier tests. They typically have rather low power for all but large samples. The tests are also affected by the unknown number of outliers present. In addition, as might be expected, they are sensitive to departures from the assumed probability distribution. They should be used only with great caution in preliminary studies where the nature of the probability distribution is largely unknown.

Testing of Hypotheses

The most commonly used test of hypotheses for comparison between two population means or for comparison of a population mean with some standard value is a t-test. To compare two means, using data from simple random samples of the two populations, the following test statistic is employed:

$$t_s = (\bar{x}_1 - \bar{x}_2)/s_p\surd[1/n_1)+(1/n_2)]$$

where, the pooled standard deviation,

$$s_p = \surd[\{(n_1-1)s_1^2+(n_2-1)s_2^2\}/(n_1+n_2-2)]$$

and x_i, s_i, and n_i are the sample mean, sample variance, and sample size for the ith (i=1,2) sample. In this two-sample t-test, one is either testing the null hypothesis, H: $\mu1 \neq \mu_2$, against the two-tailed alternative that two means are different, A: $\mu_1 \neq \mu_2$, or against a one-tailed alternative, A: $\mu_1 > \mu_2$. For the two-tailed case, one accepts the alternative hypothesis only if $|t_s| \geq t$, where t is the value found in the table of Appendix A and listed in the $1-\alpha$ column, for two-tailed tests, and the (n_1+n_2-2) (df) row. For the one-tailed alternative, one accepts the alternative hypothesis only if $t_s > t$, where t is now obtained from the same row of the table, but from the $1-\alpha$ column for one-tailed tests. Note, in the table that, "confidence level" is one minus significance level and reflects a correspondence between confidence intervals and tests for means based on the Student's t-distribution.

The one-sample t-test which compares a population mean with a standard value may arise in determining whether the mean concentration of a pollutant in a study area exceeds a specified action level. The test statistic for this test is

$$t_C = (\bar{x} - L)(\sqrt{n})/s$$

where L is the standard value (action level) and s is the sample standard deviation. One-and two-tailed tests are performed in the same way as described above for the two-sample test, except that the numbered degrees of freedom is now (n-1). In dealing with action levels one would be interested in the one-tailed test.

Example:

A preliminary study is done in an area suspected of being contaminated with polychlorinated biphenyls (PCB's). Sixteen sediment samples were collected from both the study area and from a background area through the use of simple random sampling. Table 5 lists the data and their summary statistics.

TABLE 5. PCB STUDY TO DETERMINE CONTAMINATION OF AN AREA (HYPOTHETICAL DATA)

Background Area (ppb)		Study Area (ppb)	
35.8	38.5	47.0	50.0
45.5	36.0	62.0	49.6
35.5	40.5	47.0	53.5
32.0	35.5	59.5	68.0
50.0	45.5	40.0	60.0
39.0	37.0	57.5	45.0
37.0	36.0	48.5	42.5
47.0	53.0	53.0	58.7

$\bar{x}_B = 40.23$ ppb $s_B^2 = 36.8825$ $n_B = 16$ $CV_B^* = 15.1\%$
$\bar{x}_S = 52.61$ ppb $s_S^2 = 60.2598$ $nS = 16$ $CV_S = 14.8\%$

*CV - Coefficient of variation in %

The test statistic is calculated as follows:

$$s_p = \sqrt{[15(36.8825 + 60.2598)/(16 + 16 - 2)]} = 6.97$$

$$t_s = [52.61 - 40.23]/[6.97\sqrt{(2/16)} = 5.02$$

the critical value t, for a $\alpha = 0.01$ significance level one-tailed test with 30 degrees of freedom, is found in the Appendix A table to be 2.457. The observed value of the test statistic, 5.02, is much larger than the critical value and so one would conclude that the mean level of PCB concentration in the study area is larger than that in the background area. While the difference in the two sample means was found to be statistically significant at the 1% significance level, one may still wonder whether the difference is scientifically significant in terms of potential health hazard. We can be 99% confident that the mean concentration of the study area exceeds that in the background area by

$$\bar{x}_S - \bar{x}_B - ts \surd[(1/n_B)+(1/n_S)]$$

$$= 52.61 - 40.23 - (2.457)(6.97)\surd(2/16)$$
$$= 6.28 \text{ ppb.}$$

This is a one-tailed confidence interval; $\mu_S - \mu_B \geq 6.28$ppb.)

The t-tests are based on the assumptions that the data are independent, normally distributed with equal variances, and that all observations from the same sample have the same expected value. In the two-sample t-test the assumptions of normality and equal variance may be relaxed if sample sizes are essentially equal. One-tailed one-sample t-tests on data from a non-normal skewed distribution may have probabilities of Type I and Type II errors that are considerably different from those determined on the assumption of a normal distribution. If the samples are not simple random samples but do have a random component in their selection such as in stratified random sampling, then the estimate of standard deviation and the calculation of degrees of freedom will be affected. One will use the positive square root of the ANOVA table mean square for "Samples" as the estimate (s or s_p) of standard deviation in the test statistic, and the degrees of freedom for t will be the degrees of freedom for "Samples" in the ANOVA table.

Consider again the data in Table 3 as coming from strata of equal area and suppose the action level is 3.0. The test of the hypothesis, H: $\mu = 3.0$, against the alternative, A: $\mu > 3.0$, would have test statistic,

$$\begin{aligned} tc &= (\bar{x} - 3.0)\sqrt{n}/s \\ &= (3.43 - 3.0)\sqrt{24}/\sqrt{0.3199} \\ &= 3.72 \end{aligned}$$

If a 1% significance level is to be employed, one would find in Table 1 in the column headed 99 under the one-tailed test and in the row headed 8 (df) the number 2.896. Since the observed value of the test statistic is not less than the critical value, the alternative hypothesis should be accepted; that is, the mean level of pollutant concentration is above action level.

Statistics Associated with Biological Monitoring

The statistical procedures listed above apply primarily to the direct measurement of contaminants in sediments. However, considerable research in the monitoring of water quality using benthic species counts and application of nonparametric and multivariate statistical analyses has appeared over the past 20 years. A presentation of some of the statistical procedures and some references to this literature are given by Ball, et al. (1981).

CHAPTER 5

EXPLORATORY STUDY

INTRODUCTION

Once objectives have been defined which involve the need for sediment sampling, the next step is to develop a total study protocol including an appropriate QA/QC program. Generally, not enough information or data will be available to proceed directly. The recommended approach is to conduct an exploratory study first that includes both a literature and information search along with selected field measurements made on the basis of some assumed transport model.

In order to provide a framework for the discussion, a hypothetical situation involving an abandoned hazardous waste site will be described. In this scenario there is substantial reason to believe that an abandoned waste site for hazardous chemicals is leaking chemicals into the surrounding environment which includes a few scattered farms and a medium size river which empties into an estuary of the Gulf of Mexico about twenty kilometers downstream.

The established objective for this hypothetical situation is to conduct an environmental assessment of the site and its environs to determine whether a short or long term hazard to man or the environment exists. If a hazard exists, its nature and extent must be defined and appropriate recommendations made to bring the hazard under control. Assume that a study team is organized to address this problem and that the sediment study group's task is to identify and make an assessment of potential problems associated with sediments in the river and in the estuary. Other members of the team will be concerned with soil, groundwater, and air pollution problems and their consequences. All data gathered by specific members of the team will be shared with the entire team.

Questions which must be answered by the exploratory study include but are not limited to the following:

- What wastes have been placed at the disposal site over what time periods?
- What chemicals in what amounts have escaped from the site via what transport routes and what is the present geographical extent of these chemicals?
- What adverse effects on human health or the environment have been reported in the site vicinity?
- What is an appropriate background, or control region, to use for the study?

Before taking any field measurements, a comprehensive literature and information search should be conducted to determine what information may already be available. Only after relevant information has been collected, collated, and evaluated should any field measurements be taken. The results of the exploratory study will provide information and field data that will serve as the basis for the design of a more definitive monitoring study. Thus, any field measurements taken should include appropriate QA/QC measures to determine the quality of the data.

Assume that the information and literature search elicit the following items. The wastes are from a chemical company which specialized in petrochemical products. The wastes were placed at the site beginning about forty years ago and ending about fifteen years ago when the company went out of business. Metal drums containing the wastes were covered over with a thin layer of soil prior to abandonment of the site. Some of the known constituents of the wastes have been listed as hazardous by the USEPA. Complaints from nearby residents constitute strong evidence that some of the hazardous constituents have escaped from the site in surface waters, and because the groundwater at this site is not very deep, there is reason to suspect that it too may be contaminated. No quantitative information was found on concentrations of the hazardous chemicals in soil, surface waters, groundwater, air, locally produced food, or sediments. A few recent studies in varied locations were found in which measurements for some of the hazardous chemicals of concern had been made in sediments. The coefficient of variation for these studies averaged about 30%.

NUMBER AND LOCATIONS OF SITES FOR SAMPLING

The sediment study group concludes that there is sufficient evidence to warrant conducting an exploratory study in the sediments of the nearby river. Using the guidelines suggested in Chapter 3, plus information obtained from the literature search, the following input factors are established to determine the required number of samples: CV = 30%, Confidence Level = 80%, Power = 95%, and Minimum Detectable Relative Difference = 20%. The approximate number of samples required for a one-sample one-sided t-test of the hypotheses, $H{:}\mu=L$ versus $A{:}\mu>L$ may be calculated using the following formula (Guenther, 1981)

$$n \geq [(Z_{\mu} + Z_{\beta})/D]^{2}_{\alpha} + 0.5Z^{2}$$

where Z_{α} is a percentile of the standard normal distribution such that $P(Z \geq Z_{\alpha})=\alpha$, Z_{β} is similarly defined, and

D = (minimum detectable relative difference)/CV.

Hence, for this example,

$$n \geq [(0.842+1.645)/(20/30)]^2 +0.5(0.842)^2$$

$$n \geq 13.917=0.354=14.269$$

$n = 15$ (note:always round UP)

For a two-sided one-sample t-test, determine n by replacing Z in the above formula with $Z_{\alpha/2}$; that is, in the above example replace 0.842 with 1.282 to obtain n=21.

For a one-sided two-sample t-test, the sample size for each sample should satisfy the formula,

$$n \geq 2[(Z_{\alpha} + Z_{\beta})/D]^2 +0.25Z_{\alpha}^{2}.$$

Again to obtain the corresponding minimum number for a two-sided two-sample t-test, change Z_{α} to $Z_{\alpha/2}$.

To determine the locations of these samples, the following approach is suggested. Estimate the sampling location(s) on the river closest to the waste site via the likely surface water flow. Label this spot zero on a coordinate system extending down river. Stratify the study region and locate the sampling points systematically as shown in the following sketch.

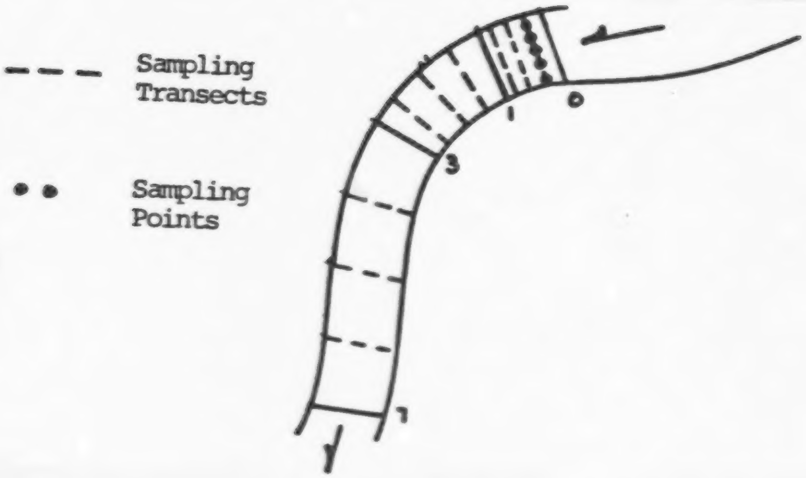

Figure 5. Sketch map of river showing stratified regions and sampling points.

The first stratum would be from 0 to 1 km, the second from 1 to 3 km, and the third from 3 to 7 km. Locate sampling transects at 1/4, 1/2, and 3/4 the distance along the river from the beginning of the stratum to its end. Locate sampling points along the transects at 1/6, 1/3, 1/2, 2/3, and 5/6 the distance from bank to bank. This provides 15 sampling points within each stratified region as required.

It is suggested that a background region be established approximately 10 km upstream from the 0 point of the river-based coordinate system and extending about 1 additional km upstream to define a region the same size as the first study stratum. The fifteen sampling points in the background region would then be located as they are in the first study stratum.

The QA/QC program for the exploratory study must be adequate for the resulting data to serve as a foundation for further studies. For our hypothetical case, it is suggested that three duplicate samples be collected from each stratified study region (to include the background region as well).

Also it is suggested that three samples from each stratified region be split into triplicate samples. It is recommended that a modest number of additional independent QA/QC sediment samples be taken at approximate mid-points between selected sampling points at locations in stratified regions in which the hypothetical model predicts the highest concentrations will be found. Data from these additional samples will give some measure of how well the QA/QC plan is achieving its objectives. In addition, all normal analytical QA/QC procedures such as field and trip blanks, etc., should be operative for the exploratory study.

SAMPLING AND SAMPLE HANDLING

An approved protocol should be followed for sampling, handling, labeling, transporting, and chain-of-custody procedures for sample containers and samples. The possible presence of volatile pollutants should be considered in the selection of an appropriate protocol. Sample volumes will be specified by the analytical laboratory depending on the analytical methods to be used and the desired sensitivity. Often, in addition to measurements of principal hazardous constituents in sediments, other chemical, physical, or biological measurements will be made for various purposes. Examples of possible additional desired measurements for either the exploratory or the definitive study are presented in Table 6.

TABLE 6. COMMON MEASUREMENTS FOR SURFACE WATER, AQUATIC ORGANISMS AND SEDIMENT SAMPLING

Chemical	Physical	Biological
Dissolved oxygen	Color	Fish
Phosphate	Turbidity	Benthic Macroinvertebrates
Nitrogen series	Water temperature	Periphyton
Alkalinity	Stream velocity	Phytoplankton
Silica	Water depth	Zooplankton
pH	Sediment composition	Macrophytes
Specific conductance		Macroalgae
Solids (TDS,TS,TSS)		Bacteria
Organic matter and demand		
Pesticides		
Heavy Metals		

Source: USEPA, 1982a

The sampling device used should be consistent with the objectives of the final study. In general, the simplest sampling tool deemed to be adequate should be used. The advantages and disadvantages of some bottom grabs/sampler and of some coring devices are presented in Tables 7 and 8, respectively. It can be seen that all methods of sediment sampling have disadvantages as well as advantages. When choosing a sampler, weigh the type of samples needed to achieve the objectives of the study against the advantages, disadvantages, and cost of the various alternatives.

Surface sampling should normally be augmented with a modest number of sediment core samples to determine how the various measured parameters vary as a function of depth. These additional samples should be located in areas in which the highest contamination levels are expected. Data from these samples will provide information for deciding if more than

TABLE 7. COMPARISON OF BOTTOM GRABS/SAMPLERS

Device	Advantages	Disadvantages
Ponar	Safe, easy to use, prevents escape of material with end plates, reduces shock wave, combines advantages of others, preferred grab in most cases	Can become buried in soft sediments
Ekmann	Use in soft sediments and calm waters, collects standard size sample (quantitative), reduces shock wave	Not useful in rough water; not useful if vegetation on bottom
Tall Ekman	Does not lose sediment over top; use in soft sediments and calm water, standard sample size, reduces shock wave	Not useful in rough waters, others as for Ekman
Peterson	Quantitative samples in fine sedients, good for hard bottoms and sturdy and simple construction	May lose sampled material, premature tripping, not easy to close; does not sample constant areas; limited sampling capacity
Smith-Mcintyre	Useful in bad weather, reduces premature tripping, use in depths up to 1500 m (3500 ft), flange on jaws reduces material loss, screen reduces shock waves, good in all sediment types	Large, complicated and heavy, hazardous for samples to 7 cm depth only, shock wave created
Diver	Can determine most representative sampling point and current velocity	Requires costly equipment and special training

Source: USEPA, 1982a

TABLE 8. COMPARISON OF CORING DEVICES

Device	Advantages	Disadvantages
Kajak or K. B. Corer	Does not impede free flow of water, no pressure wave, easily applied to large area	
Moore (Pfleger)	Valve allows sample to be held	Careful handling necessary to avoid sediment rejection, not in soft sediments
O'Conner	Can sample water with hard bottoms	Not in deep water
Elgmork's	Sample easily removed, good in soft muds, easy to collect, easty to remove sample	Not in hard sediments
Jenkins	Good in soft sediments and for collecting an undisturbed sediment-water interface sample. Visual examination of benthic algal growth and rough estimates of mixing near the interface after storms can be made	Complicated
Enequist	Good in soft/medium sediments, closing mechanism	Does not penetrate hard bottom
Kirpicenko	Soft and hard bottoms, various sizes, closes automatically	Not for stony bottoms

Source: USEPA, 1982a

surface sediments need to be sampled in the final definitive study.

Additional concerns in sampling design include whether samples should be composited, frequency of sampling, sample preparation for analyses, and the QA/QC aspects of all of these parameters. The exploratory study provides a limited opportunity to investigate some of the above subject areas.

The major concerns with regard to compositing of sediment samples are that the samples be representative and that high concentrations not be cancelled out in the calculation of the mean by being averaged with too many low-level samples. The best approach usually is not to composite unless there is adequate justification for doing otherwise. The exploratory study cannot be designed to obtain information on temporal patterns in sediment concentrations since the study must be completed in a relatively short period of time. Thus, temporal trends should be addressed in the final study.

Sample preparation for analyses introduces some possibilities for errors. The sample preparation may involve drying, grinding, mixing, or sieving. Also, prior to sample preparation, non-sediment material may be removed from the collected sediment sample. Any equipment or devices used in sample preparation must be carefully cleaned between each sample to avoid cross-contamination. The final rinse fluid used for cleaning equipment should be sampled to provide a decontamination sample blank for use in evaluating the cleanup efficiency. Collection of one sample blank after processing each 20 samples has been used successfully in some EPA studies (USEPA 1982, 1984).

One of the possibilities for error during the sampling process is discarding non-sediment material collected with the sediment sample prior to analysis. It is suggested that all such discarded material be retained. Ten percent of these samples should be sent to the analytical laboratory for analysis with the remainder being archived. Care must be taken in evaluating and interpreting these data as data quality will be a function of analytical capability.

In order to make this report more self-contained, the enter chapter on Sample Handling and Documentation from the companion soil document (Barth and Mason, 1984) is included in Appendix B.

ANALYSIS AND INTEPRETATION OF DATA

Analysis and interpretation of all information and data resulting from the exploratory study will provide the basis for designing the final definitive monitoring study including all elements of the QA/QC plan. For example, decisions must be made on whether the selected control area is adequate; whether the hypothesized model is valid; whether the study area should be stratified in a different way; what number of additional samples should be collected at what locations; whether the QA/QC plan for sampling is adequate; etc. All deficiencies or errors detected should be corrected in the final study design.

If the exploratory study is conducted well, it will provide some data for achieving the objectives of the study; it will provide data concerning the feasibility and efficacy of most aspects of the study design including the QA/QC plan; it will serve as a training vehicle for all participants; it will pinpoint where additional measurements need to be made; and it will provide a body of information and data for incorporation into the final report for the total study.

A summary of some assumed results from an exploratory study for the specific hypothetical case posed in this chapter will be provided at the beginning of the next chapter. These results will then be used to indicate corrections and additions needed for the final definitive study.

CHAPTER 6

FINAL DEFINITIVE STUDY

INTRODUCTION

Following analysis and interpretation of the information and data resulting from the exploratory study the next step is the design of the final definitive study. Any problems with the QA/QC plan noted during the exploratory study should also be solved by appropriate modifications of the plan. The procedure will be illustrated by extending the hypothetical case study defined in Chapter 5. To do this it is necessary to present some assumed summary results from the exploratory study. Accordingly, Table 9 gives mean values and standard deviations obtained in the various stratified regions and in the background, or control region, for the principal hazardous constituent deemed to be critical in the sense of posing the greatest potential danger to man or the environment. The units are parts per billion in the sediments by weight.

TABLE 9. SUMMARY OF SELECTED HYPOTHETICAL RESULTS FROM THE EXPLORATORY STUDY.

Region (Stratum)	Background(15)*	1(15)	2(15)	3(15)
Mean (ppb)	1.24	13.2	15.1	11.5
CV (%)	30.3	45.2	40.7	47.6

Samples taken at different depths in Region 1

Depth	Mean (pphm)	CV(%)
0-4 in (5)	14.8	48.1
4-8 in (5)	5.21	52.4
8-12 in (5)	1.75	56.7

* Numbers of samples in parentheses.

Assume that three duplicates and three triplicates were taken in each of the stratified regions as part of the QA/QC plan for the exploratory study and that the resulting data confirmed the adequacy of two duplicates and two triplicates per stratified region. All normal analytical QA/QC procedures were in force and no problems were identified. Other sampling efforts confirmed the presence of the contaminant measured in sediments in surface water, groundwater, soil and selected foods, with the largest concentrations observed close to the hazardous waste site. Analysis of variance of the sediment data showed that in excess of 70% of the total variance was due to location.

Returning to an evaluation of the hypothetical results shown in Table 9 allows certain tentative conclusions to be drawn.

- Sediments are sufficiently contaminated to be a cause for concern.

- The background area selected is adequate (The mean determined is close to other reported background levels).
- The implicit hypothesized model which expected the highest mean concentration to be in Region 1 is questionable since Region 2 had a slightly higher mean.
- The mean value for Region 3 suggests that sediments farther downstream are likely to be significantly contaminated.
- The depth measurements taken suggest that only the top 8 inches of sediments may be contaminated significantly.

In view of these conclusions certain matters will need to be clarified in the definitive study. Some questions which should be answered include the following:

- How far down stream are the sediments significantly contaminated?
- What are the relative contributions of surface water and groundwater to the contamination of sediments?
- How are the sediment levels changing as a function of time?
- What are the levels of contamination in human foods derived directly or indirectly through contact with sediments?
- What is the impact of contaminated sediments on aquatic biota?
- How should the study area be stratified in the definitive study?

These questions will be discussed at some length in subsequent sections of this chapter.

It is likely that for a situation of this type an emergency action level, as well as a long term residual level, would be specified by a decision-making official if none exists. The most likely media for such an action limit would be drinking water and/or foods. Such an approach would require that a model be available or developed to link contaminant levels in sediments to drinking water and/or food levels. Such a derived level in sediments might be used as an operational action level.

SELECTION OF NUMBERS OF SAMPLES AND SAMPLING SITES

Assume that, after careful consideration of all available information, a decision official has come to the conclusion that emergency action is not warranted but a remedial response operation is called for. Referring back to Chapter 4, recommended values for confidence level, power, and minimum detectable relative difference are 90-95%, 90-95%, and 10-20%, respectively. Table 11 presents the numbers of samples required to achieve these values for different coefficients of variation (CV). Table 10 below summarizes the situation over the range of the recommended values for an assumed average CV of 25%. This assumes that the CVs measured in the exploratory study can be reduced by more judicious stratification of the study region.

Table 10. NUMBER OF SAMPLES REQUIRED PER STRATIFIED REGION AS A FUNCTION OF INDICATED PARAMETERS.

Confidence Level	Power	Minimum Detectable Relative Difference	No. of Samples
95%	95%	10%	$\geq$ 69
95%	90%	20%	$\geq$ 19
90%	95%	20%	$\geq$ 15
90%	90%	20%	$\geq$ 12

The decision-making official decides to go with a confidence level of 90%, a power of 95%, and a minimum

TABLE 11. NUMBER OF SAMPLES REQUIRED IN A ONE-SIDED ONE-SAMPLE t-TEST TO ACHIEVE A MINIMUM DETECTABLE RELATIVE DIFFERENCE AT CONFIDENCE LEVEL (1-α) AND POWER OF (1-β).

Coefficent of Variation (%)	Power (%)	Confidence Level (%)	Minimum Detectable Relative Difference (%)				
			5	10	20	30	40
10	95	99	66	19	7	5	4
		95	45	13	5	3	3
		90	36	10	3	2	2
		80	26	7	2	2	1
	90	99	55	16	6	5	4
		95	36	10	4	3	2
		90	28	8	3	2	2
		80	19	5	2	1	1
	80	99	43	13	6	4	4
		95	27	8	3	3	2
		90	19	6	2	2	2
		80	12	4	2	1	1
15	95	99	145	39	12	7	5
		95	99	26	8	5	3
		90	78	21	6	3	3
		80	57	15	4	2	2
	90	99	120	32	11	6	5
		95	79	21	7	4	3
		90	60	16	5	3	2
		80	41	11	3	2	1
	80	99	94	26	9	6	5
		95	58	16	5	3	3
		90	42	11	4	2	2
		80	26	7	2	2	1
20	95	99	256	66	19	10	7
		95	175	45	13	9	5
		90	138	36	10	5	3
		80	100	26	7	4	2
	90	99	211	55	16	9	6
		95	139	36	10	6	4
		90	107	28	8	4	3
		80	73	19	5	3	2
	80	99	164	43	13	8	6
		95	101	27	8	5	3
		90	73	19	6	3	2
		80	46	12	4	2	2

TABLE 11. CONTINUED.

Coefficent of Variation (%)	Power (%)	Confidence Level (%)	Minimum Detectable Relative Difference (%)				
			5	10	20	30	40
25	95	99	397	102	28	14	9
		95	272	69	19	9	6
		90	216	55	15	7	5
		80	155	40	11	5	3
	90	99	329	85	24	12	8
		95	272	70	19	9	6
		90	166	42	12	6	4
		80	114	29	8	4	3
	80	99	254	66	19	10	7
		95	156	41	12	6	4
		90	114	30	8	4	3
		80	72	19	5	3	2
30	95	99	571	145	39	19	12
		95	391	99	26	13	8
		90	310	78	21	10	6
		80	223	57	15	7	4
	90	99	472	120	32	16	11
		95	310	79	21	10	7
		90	238	61	16	8	5
		80	163	41	11	5	3
	80	99	364	84	26	13	9
		95	224	58	16	8	5
		90	164	42	11	6	4
		80	103	26	7	4	2
35	95	99	775	196	42	25	15
		95	532	134	35	17	10
		90	421	106	28	13	8
		80	304	77	20	9	6
	90	99	641	163	43	21	13
		95	421	107	28	14	8
		90	323	82	21	10	6
		80	222	56	15	7	4
	80	99	495	126	34	17	11
		95	305	78	21	10	7
		90	222	57	15	7	5
		80	140	36	10	5	3

detectable relative difference of 20%. Accordingly, a minimum of 15 samples will be required per stratified region which by chance happens to be the same number of samples used in the exploratory study. Additional QA/QC samples necessary have been indicated in Table 4, Chapter 4. It is suggested that fifteen additional depth samples be taken in Region 2 in the same fashion as they were taken in Region 1 in the exploratory study.

In deciding on how to stratify the study region for the more definitive study, the information gained in the exploratory study should be used. Since the means in Regions 1 and 2 for the exploratory were almost equal, it seems justified to combine them into a single region. Thus, the suggested new stratified regions are as shown in Table 12 below.

TABLE 12. NEW STRATIFIED REGIONS FOR THE MORE DEFINITIVE STUDY.

Region A	Region B	Region C
0 - 3 km	3 - 9 km	9 - 21 km

Note: All regions now extend only from the near bank to the middle of the river. See discussion below.

Note that the estuary into which the study river flows is 20 km from the 0 point of the river coordinate system. Thus, Region C extends 1 km from the mouth of the river into the estuary.

Location of sampling sites within the stratified regions is the next order of business. Assume that analysis of data from the exploratory study showed consistently that sampling points from the middle of the river channel to the far bank gave much lower levels than the other sampling points. This finding serves as the basis for altering both the stratification and the sampling site selection process for the more definitive study into study regions extending only from the near bank to the middle of the river channel.

Also, note that combining old Regions 1 and 2 into new Region A means that 12 measurements (the other 18 obtained are now outside Region 4) are already available in Region A from the exploratory study. It is recommended that 6 additional samples be taken in Region A at sites 1/12 and 1/4 the distance along the three sampling transects used for the exploratory study. Region B contains 6 measurements from the exploratory study, but with no measurements beyond kilometer 6. It is suggested that 4 additional measurements (at sites 1/12, 1/6, 1/4, and 1/3 the distance along the cross-river transects) be made at kilometers 7 and 8. In addition, 6 additional samples should be taken in Region B at sites 1/12 and 1/4 the distance along the sampling transects used for the exploratory study. This will give a grand total of 20 measurements for Region B. For Region C it is suggested that 4 samples each be taken along transects (at sites 1/12, 1/6, 1/4, and 1/3 the distance across the river) located at kilometers 11, 14, 17 and 20 and that 4 samples each be collected in the estuary at sites 1/12, 1/6, 1/4, and 1/3 the distance from the near shore and along arcs centered at the mouth of the river and at distances of 1/2 and 1 km. This will provide a total of 24 samples for Region C. The plan proposed thus calls for the collection of 44 additional samples. The extra samples suggested for Region C are to get a better estimate of the contamination of sediments in the estuary.

Coordination would have to be established with water and food sampling teams to assure that they direct a portion of their more definitive study efforts to obtaining measurements in water and food which might be related to sediment measurements. It would be particularly important to obtain samples of seafood harvested in the estuary.

Similarly, coordination would have to be established with aquatic biologists assessing the impact of sediment contaminants or aquatic biota. Particular attention should be paid to assessing effects of the contaminants on juvenile populations of human food species as well as reproductive success of the same species.

So far no attention has been given to the question concerning relative contributions of surface water and groundwater to the contamination of sediments. Perhaps data obtained by the teams measuring these media close to the hazardous waste site will provide some important evidence. Geophysical remote sensing measurement tools may help to delineate the groundwater hydraulic gradient and patterns of groundwater flow in the vicinity. Also, estimates of total contributions to contamination of sediments taken together with estimates of surface water contributions enable the groundwater contributions to be estimated by taking the difference between these two values. It is particularly important to have an estimate of the groundwater contribution and how it varies as a function of time in order to evaluate the likely success of different control options.

Sample collection, sample handling, and documentation must be done in accordance with an established protocol. In this instance, the same procedures used in the exploratory study should be applicable to and adequate for the more definitive study. If problems have been detected in the exploratory study, appropriate modifications must be made to solve these problems prior to proceeding with the more definitive study. Table 13 contains some suggestions for sampling containers, preservation requirements, and holding times for sediment samples. Audits are perhaps the most effective tool to ensure that all aspects of sample collection, sample handling and documentation are being accomplished according to the approved protocol (See Appendix D and USEPA, 1985).

The required frequency of sampling depends on the objectives of the study, the sources and sinks of pollution, the pollutant of concern, transport rates and disappearance rates (physical, chemical, or biological transformations as

Table 13. Sampling Containers, Preservation Requirements, and Holding Times for Sediment Samples

CONTAMINANT	CONTAINER	PRESERVATION	HOLDING TIME
Acidity	P,G	Cool, 4°C	14 days
Alkalinity	P,G	Cool, 4°C	14 days
Ammonia	P,G	Cool, 4°C	28 days
Sulfate	P,G	Cool, 4°C	28 days
Sulfide	P,G	Cool, 4°C	28 days
Sulfite	P,G	Cool, 4°C	48 hours
Nitrate	P,G	Cool, 4°C	48 hours
Nitrate-Nitrite	P,G	Cool, 4°C	28 days
Nitrite	P,G	Cool, 4°	48 hours
Oil and Grease	G	Cool, 4°C	28 days
Organic Carbon	P,G	Cool, 4°C	28 days
Metals			
Chromium VI	P,G	Cool, 4°C	48 hours
Mercury	P,G		28 days
Metals except above	P,G		6 months
Organic Compounds			
Extractables (including phthalates, nitrosamines organochlorine pesticides, PCB's nitroaromatics, isophorone, Polynuclear aromatic hydrocarbons, haloethers, chlorinated hydrocarbons and TCDD)	G, teflon-lined cap	Cool, 4°C	7 days (until extraction) 30 days (after extraction)
Extractables (phenols)	G, teflon-lined cap	Cool, 4°C	7 days (until extraction) 30 days (after extraction)
Purgables (halocarbons and aromatics)	G, teflon-lined septum	Cool, 4°C	14 days
Purgables (acrolein and acrylonitrate)	G, teflon-lined septum	Cool, 4°C	3 days
Orthophosphate	P,G	Cool, 4°C	48 hours
Pesticides	G, teflon-lined cap	Cool, 4°C	7 days (until extraction) 30 days (after extraction)
Phenols	P,G	Cool, 4°C	28 days
Phosphorus (elemental)	G	Cool, 4°C	48 hours
Phosphorus, total	P,G	Cool, 4°C	28 days
Chlorinated organic compounds	G, teflon-lined cap	Cool, 4°C	7 days (until extraction) 30 days (after extraction)

Polyethylene(P) or Glass(G)

Sample preservation should be performed immediately upon sample collection. For composite samples each aliquot should be preserved at the time of collection. When impossible to preserve each aliquot, then samples may be preserved by maintaining at 4°C until compositing and sample splitting is completed.

Samples should be analyzed as soon as possible after collection. The times listed are the maximum times that samples may be held before analysis and still considered valid. Samples may be held for longer periods only if the analytical laboratory has data on file to show that the specific types of samples under study are stable for the longer time.

For additional information see Ford et al. (1983).

well as dilution or dispersion by any other means). Sampling frequency may be related to changes over time, season, or precipitation. Little information will be available on sampling frequency from exploratory study data. However, these data will provide baseline information at a given point in time from which future trends may be measured. Assessment of future trends will establish whether sediment concentrations are increasing, decreasing, or remaining fairly level. Evaluation of these trends will be important to selection of appropriate remedial response measures or to the determination that remedial response measures will not be required.

The recommended procedure for establishing time trends is to sample monthly for the first year. Evaluation of the trend of the data will then enable a determination to be made concerning possible changes in sampling frequency. If the only concern is for time trends in each stratified study region, then compositing 15 or more samples from each region for each monthly sample may be the simplest way to proceed. On the other hand, if the changing of spatial patterns with time is of interest, the compositing approach would not be recommended. In the latter case, the time trends for changes in individual samples at definite locations would be needed. Thus the preferred approach would be to repeat the sampling program previously described at monthly intervals until sufficient data accumulate to justify changing the sampling frequency intervals. The major focus should be on the highly contaminated and immediately adjacent areas.

Quality assurance/quality control procedures for frequency of sampling validation may be accomplished through techniques such as trend line or interdiction analysis. Also, the taking of initial samples on a frequency considered to be more often than is likely to be required may provide some redundant data but will assist in verifying the adequacy of the sampling plan. A comparison between the first samples taken and the most recently collected samples should show a decrease in pollutant concentrations unless there is a new source of pollutants, there is migration into the sampled sediments, there is an error in the data, or the decrease is not sufficient to be resolved due to the variability of sample data. This test becomes a better indicator the longer the study runs.

The analysis and interpretation of QA/QC data from the more definitive study should show how all aspects of the total QA/QC plan combine to give an overall level of reliability for various aspects of the resulting data. Another goal may be to determine whether all QA/QC procedures used were necessary and adequate. This entire evaluation must be closely linked to the objectives of the study. In summary the important questions to be answered are, "What is the quality of the data?" and "Could the same objective have been achieved through an improved QA/QC design which may have required fewer resources?"

It is desirable to provide summarized tables of validated QA/QC data in the final report. For example, QA/QC data validation procedures used in a number of soil sampling studies reported by Brown and Black (1983) included validation of sample data sets by checking and assessing the accompanying QA/QC data. In order to make this report more self-contained, the entire chapter on analysis and interpretation of QA/QC data from the companion soil document (Barth and Mason, 1984) is included in Appendix C. This approach is equally applicable for sediment sampling data. The criteria for QA/QC samples and procedures used to validate all data should be clearly stated.

From such tables of validated QA/QC data it is possible to determine bias, precision (total random error), component random errors associated with reproducibility, extract matrix, sample matrix, and sample homogeneity, interlaboratory precision, and uncertainty.

Presentation of QA/QC data allows readers to verify conclusions drawn as to reliability of the data. Such presentation also contributes to the building of a body of QA/QC data in the literature which allows comparison to be made between and among studies. Special emphasis should be placed on explaining how overall levels of precision and confidence were derived from the data.

As a final check, the adequacy of all aspects of the QA/QC plan should be examined in detail with emphasis on defining for future studies an appropriate minimum adequate plan. Some aspects of the plan actually used may have been too restrictive, while others may not have been restrictive enough. Appropriate analyses and interpretation of the data should identify the actual situation.

There is insufficient knowledge dealing with sediment monitoring studies to state with confidence which portions of the QA/QC plan will be generally applicable to all sediment monitoring studies and which portions must be varied depending on site-specific factors. As experience is gained, it may be possible to provide more adequate guidance on this subject. In the meantime, it is recommended that the best approach is to assume that important factors of QA/QC plans may be site specific and to conduct an appropriate exploratory study at each new study site to verify that various aspects of the QA/QC plan are adequate to meet program objectives prior to proceeding with the final definitive study.

In lieu of providing hypothetical data resulting from the more definitive study, a brief general discussion will be provided indicating possible conclusions which might be drawn from the data. Comparison of the calculated means and standard deviations for each stratified study region to any assigned action level by appropriate statistical methods outlined in Chapter 4 will establish which stratified regions presently have concentrations exceeding acceptable limits. If action levels are only specified for drinking water and foods, then an estimated comparable action level for sediments must be derived from an appropriate model.

If time trend analyses indicate that concentrations in sediments are increasing with time, peak values have not yet been achieved. In this case, available data from the study teams should be combined with alternative control options and an appropriate model to predict when and where the maximum future values will be found as well as their estimated peak concentrations.

If time trend analyses indicate that concentrations in sediment are decreasing with time, projected values for the future should be predicted by combining data from their study teams with alternative control options and an appropriate model. If the trends show concentrations decreasing rapidly enough, there may be no necessity for control actions.

The case in which time trends show fairly constant values, or sometimes increasing and sometimes decreasing ones, should be treated similarly to the case in which concentrations are increasing with time.

For the more definitive study, additional measurements in sediments over and above the concentrations of the hazardous waste of concern should include as a minimum the following for each sampling period:

Depth of the river
Flow rate
Suspended solids
Bed load
pH
Temperature
Living species populations and diversity in sediments
Body burdens of the hazardous waste for selected species dwelling in sediments
Adverse effects on selected species dwelling in sediments

The purpose of these extra measurements, in addition to their intrinsic value, is to validate existing sediment transport models or provide data on the basis of which modifications may be made in existing models or new models may be developed. The biological measurements may assist in either defining adverse effects on sediment biota or in providing information for linking contamination in sediment biota to contamination in human foods via models.

Data from the more definitive study describing variations in sediment concentrations with depth will show how effective dredging to different depths might be in the removal of the contamination. If dredging is even contemplated, safe and effective methods for disposing of the dredge spoil must be available.

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APPENDIX A

PERCENTILES OF THE T DISTRIBUTION

	Confidence Level (%):$100(1-\alpha)$ for two-tailed test							
	20	40	60	80	90	95	98	99
	Confidence Level (%):$100(1-\alpha)$ for one-tailed test							
df	60	70	80	90	95	97.5	99	99.5
1	.325	.727	1.376	3.078	6.314	12.706	31.821	63.657
2	.289	.617	1.061	1.886	2.920	4.303	6.965	9.925
3	.277	.584	.978	1.638	2.353	3.182	4.541	5.641
4	.271	.569	.941	1.533	2.132	2.776	3.747	4.604
5	.267	.559	.920	1.476	2.015	2.571	3.365	4.032
6	.265	.553	.906	1.440	1.943	2.447	3.143	3.707
7	.263	.549	.896	1.415	1.895	2.365	2.998	3.499
8	.262	.546	.889	1.397	1.860	2.306	2.896	3.355
9	.261	.543	.883	1.383	1.833	2.262	2.821	3.250
10	.260	.542	.879	1.372	1.812	2.228	2.764	3.169
11	.260	.540	.876	1.363	1.796	2.201	2.718	3.106
12	.259	.539	.873	1.356	1.782	2.179	2.681	3.055
13	.259	.538	.870	1.350	1.771	2.160	2.650	3.012
14	.258	.537	.868	1.345	1.761	2.145	2.624	2.977
15	.258	.536	.866	1.341	1.753	2.131	2.602	2.947
16	.258	.535	.865	1.337	1.746	2.120	2.583	2.921
17	.257	.534	.863	1.333	1.740	2.110	2.567	2.898
18	.257	.534	.862	1.330	1.734	2.101	2.552	2.878
19	.257	.533	.861	1.328	1.729	2.093	2.539	2.861
20	.257	.533	.860	1.325	1.725	2.086	2.528	2.845
21	.257	.532	.859	1.323	1.721	2.080	2.518	2.831
22	.256	.532	.858	1.321	1.717	2.074	2.508	2.819
23	.256	.532	.858	1.319	1.714	2.069	2.500	2.807
24	.256	.531	.857	1.318	1.711	2.064	2.492	2.797
25	.256	.531	.856	1.316	1.708	2.060	2.485	2.787
26	.256	.531	.856	1.315	1.706	2.056	2.479	2.779
27	.256	.531	.855	1.314	1.703	2.052	2.473	2.771
28	.256	.530	.855	1.313	1.701	2.048	2.467	2.763
29	.256	.530	.854	1.311	1.699	2.045	2.462	2.756
30	.256	.530	.854	1.310	1.697	2.042	2.457	2.750
40	.255	.529	.851	1.303	1.684	2.021	2.423	2.704
60	.254	.527	.848	1.296	1.671	2.000	2.390	2.660
120	.254	.526	.845	1.289	1.658	1.980	2.358	2.617
∞	.253	.524	.842	1.282	1.645	1.960	2.326	2.576

APPENDIX B

SAMPLE HANDLING AND DOCUMENTATION

INTRODUCTION

The goal is to define the segment of the QA/QC plan dealing with all aspects of sample handling including the transfer of the sample from the collecting device to a suitable container, transportation of the sample, and the preparation of the sample for analysis. The importance of all these aspects of sample handling and possible errors introduced thereby will naturally vary with the sampling methods, monitoring objectives, characteristics of the soil being sampled and the physical and chemical properties of the pollutants of concern.

CONTAINER PREPARATION, LABELING, PRESERVATION, AND SAMPLE PREPARATION

The sampling protocol and the QA/QC plan must address the following factors.

- Type of container material, its size, shape and the type of lid.
- Cleaning procedures for the containers
- Decontamination procedures for sampling instruments.
- Decontamination procedures for sample bank equipment.
- Labeling scheme and log book entries
- Chain of custody procedures
- Sample preparation procedures in the field
- Sample preparation procedures at the sample bank

Due to a lack of specifically tested and recommended methods dealing with the storage, handling, construction and types of containers, cleaning and decontamination of containers, and suggested materials for container lids for soil samples it is suggested that the specifications and methods identified in USEPA, Federal Register Vol. 44 No. 233 (1979) be utilized.

Table B-1 provides general information on recommended containers, preservation requirements, and holding times for measuring selected contaminants. Even though these procedures and methods were specifically designed and tested for water samples, they are applicable for soil sampling studies.

For sampling studies that require a large number of samples and/or extensive preanalytical sample preparation a sample bank may be established. The sample bank is the element that operates between the field sampling effort and the analytical laboratory. However, for smaller studies the sample banks responsibilities are often incorporated into the responsibilities of the field sampling team or the analytical laboratory.

If a sample bank is established, sample bank personnel can assume responsibility for the following procedures:

- Custodian for all records pertaining to the sampling, sample preparation as required, and shipment of soil samples to analytical laboratories.

- Responsibility for record filing and storing, for storing and preparation of soil samples, and for dispensing containers, sampling equipment and all custody documents such as chain-of-custody forms and sample collection and analytical tags, as required.

- Responsibility for updating and maintaining the projects' master log book, auditing the records as required, generating sample bank QC sample blanks, accepting QA/QC samples for inclusion into the analytical scheme, and for scheduling the collection of field sample blanks.

- Responsibility for completing, as required, analysis data reporting forms and for assuring that all chain-of-custody requirements pertaining to all field sampling, shipping and sample bank operations, are adhered to.

Table B-1 Sampling Containers, Preservation Requirements, and Holding Times for Soil Samples

CONTAMINANT	CONTAINER	PRESERVATION	HOLDING TIME
Acidity	P,G	Cool, 4°C	14 days
Alkalinity	P,G	Cool, 4°C	14 days
Ammonia	P,G	Cool, 4°C	28 days
Sulfate	P,G	Cool, 4°C	28 days
Sulfide	P,G	Cool, 4°C	28 days
Sulfite	P,G	Cool, 4°C	48 hours
Nitrate	P,G	Cool, 4°C	48 hours
Nitrate-Nitrite	P,G	Cool, 4°C	28 days
Nitrite	P,G	Cool, 4°	48 hours
Oil and Grease	G	Cool, 4°C	28 days
Organic Carbon	P,G	Cool, 4°C	28 days
Metals			
Chromium VI	P,G	Cool, 4°C	48 hours
Mercury	P,G		28 days
Metals except above	P,G		6 months
Organic Compounds			
Extractables (including phthalates, nitrosamines organochlorine pesticides, PCB's nitroaromatics, isophorone, Polynuclear aromatic hydrocarbons, haloethers, chlorinated hydrocarbons and TCDD)	G, teflon-lined cap	Cool, 4°C	7 days (until extraction) 30 days (after extraction)
Extractables (phenols)	G, teflon-lined cap	Cool, 4°C	7 days (until extraction) 30 days (after extraction)
Purgables (halocarbons and aromatics)	G, teflon-lined septum	Cool, 4°C	14 days
Purgables (acrolein and acrylonitrate)	G, teflon-lined septum	Cool, 4°C	3 days
Orthophosphate	P,G	Cool, 4°C	48 hours
Pesticides	G, teflon-lined cap	Cool, 4°C	7 days (until extraction) 30 days (after extraction)
Phenols	P,G	Cool, 4°C	28 days
Phosphorus (elemental)	G	Cool, 4°C	48 hours
Phosphorus, total	P,G	Cool, 4°C	28 days
Chlorinated organic compounds	G, teflon-lined cap	Cool, 4°C	7 days (until extraction) 30 days (after extraction)

Polyethylene(P) or Glass(G)

Sample preservation should be performed immediately upon sample collection. For composite samples each aliquot should be preserved at the time of collection. When impossible to preserve each aliquot, then samples may be preserved by maintaining at 4°C until compositing and sample splitting is completed.

Samples should be analyzed as soon as possible after collection. The times listed are the maximum times that samples may be held before analysis and still considered valid. Samples may be held for longer periods only if the analytical laboratory has data on file to show that the specific types of samples under study are stable for the longer time.

For additional information see Ford et al (1983).

The following sample bank procedures have been used successfully on a number of soil monitoring studies.

A. Issuing Supplies:

(1) The sample bank issues as required sample containers, sample collection tags, chain-of-custody forms and site description forms to the sampling teams. Sample collection tags and chain-of-custody forms are normally accountable documents; the sample bank will log the forms by numerical lot identifying the team and/or the individual responsible for the temporary custody of these documents.

(2) The sample bank may be required to store sampling equipment in a suitable environment. If sampling equipment is stored at the sample bank, issuing this equipment to the sampling teams as required will be necessary.

B. Accepting and Logging Samples:

(1) Transfer of sample custody from the sampler to sample bank personnel will normally occur at the sample bank.

(2) Before accepting custody of any samples, sample bank personnel must check all tags and forms for legibility and completeness.

(a) All individual samples must have a completely filled out sample collection tag attached.

(b) Every sample must be identified on the chain-of-custody form.

(c) Each site sampled must have a completely filled out site description form.

(d) Any discrepancy will be corrected before sample bank personnel will assume custody. If a discrepancy exists that cannot be resolved to the satisfaction of the sample bank personnel, resampling, filling out additional tags and forms, and/or revisiting the site to obtain necessary documentation may be required.

(e) All unused accountable documents as shown in Table B-2 must be returned to the sample bank on a daily basis. However, depending upon circumstances such as a sampling team's schedule and route, accountable documents may be retained by the sampling team leader. The sample bank supervisor, however, must be aware of the situation.

(3) After the sampler relinquishes custody and the sample bank personnel assumes custody of the samples, each sample must be logged into the master log book.

Preparation of soil samples for analysis may require sample bank personnel to dry, sieve, mix and aliquot samples appropriately. The preparation procedures selected are determined by the contaminant to be measured and the analytical requirements. Various techniques and methods for mixing and compositing soils have been described by Oregon State University (1971), USEPA (1984), and Peterson and Calvin (1965).

It is inappropriate to initiate a sampling study without first consulting with analytical personnel. Collecting samples that cannot be suitably analyzed will not provide data necessary for satisfying the sampling objectives.

There is the possibility of errors being introduced in sample preparation procedures involving the discarding of non-soil material or of non-sieved material as well as possible losses during any grinding or drying operation. The definitive study decisions concerning the non-soil fraction must be made on the basis of the data obtained from the exploratory study. For example, available data may indicate that significant contamination is in the discarded portion. If so, it is recommended that the discarded portion from ten percent of the samples collected from the area having the highest concentrations be analyzed. An estimate can then be made of the total amount of contamination being discarded by multiplying the measured concentration in the discarded material by the total amount of the discarded material. Assuming that this amount is uniformly distributed through the soil sample remaining after non-soil materials and non-sieved materials have been discarded, one can then calculate an estimated value for the potential soil sample total concentration if none of the contamination had been discarded. Comparison of this potential concentration to the actual measured concentration will enable an estimate of the possible error to be made.

TABLE B-2. ACCOUNTABLE DOCUMENT CONTROL REQUIREMENTS

Documentation	Issued by	Numbering	Interim Responsibility	Final Responsibility
Sample Collection Tags	Sample Bank	Preserialized	Sampling Team	Sample Bank
Custody Records	Sample Bank	Preserialized	Sampling Team	Sample Bank
Field Logbooks	Sample Bank		Sampling Team	Sample Bank
Site Description Forms	Sample Bank		Sampling Team	Sample Bank
Analytical Sample Tags	Sample Bank	Preserialized	Sample Bank	Analytical Laboratory
Laboratory Notebooks	Laboratory		Analytical Laboratory	Sample Bank
Analytical Data Sheets	Sample Bank		Analytical Laboratory	Sample Bank

If the error estimated by this process exceeds acceptable limits specified in the QA/QC plan, it might be necessary to modify sample preparation procedures for the definitive study. One might consider a sample preparation procedure in which the entire collected sample (soil and non-soil materials) is extracted in the analytical laboratory. The analytical results could then be reported as amounts of contaminant per gram of mixed material. At present there is no acceptable method for proceeding in cases such as these. One problem is the lack of standard reference materials for determining and measuring errors in extraction efficiency. One solution may be to try different methods of extraction and compare the results. The final interpretation of the data must then take into consideration these estimated errors.

QUALITY ASSURANCE ASPECTS

The problem is to quantitate overall errors. The recommended procedure for verifying that the QA/QC plan is being carried out properly for this chapter's factors is a periodic audit, combined with a modest amount of extra samples and analyses related to factors discussed above.

APPENDIX C

ANALYSIS AND INTERPRETATION OF QA/QC DATA

INTRODUCTION

One goal in the analysis and interpretation of data is to show how all aspects of QA/QC for a soil monitoring study combine to give an overall level of precision and confidence for the data resulting from the study. Another goal may be to determine whether all QA/QC procedures which were used were necessary and adequate and should definitely be incorporated into future studies of the same type. This entire evaluation must be closely linked to the objectives of the study. In summary the important questions to be answered are, "What is the quality of the data (maximum accuracy attainable)?" and also," Could the same objective have been achieved through an improved QA/QC design which may have required fewer resources?"

PRESENTATION OF DATA SUMMARIES

It is desirable to provide summarized tables of validated QA/QC data in the final report. For example, QA/QC data validation procedures used in a number of soil sampling studies reported by Brown and Black (1983) included validation of sample data sets by checking and assessing the accompanying QA/QC data. The criteria for QA/QC samples and procedures used to validate all data included:

Samples and Procedures	Example Criteria
1. Reagent Blanks	Concentrations had to be less than 0.25 g/ml^{-1}.
2. Calibration Check Standards	Recovery must be between 95% and 105% of the known value for either the first analysis or the first re-check analysis.
3. Laboratory Control Standards	Recovery must be between 90% and 110% of the known value for either the first analysis or the first re-check analysis.

Data produced by any sampling and analyzing system are affected by two types of errors; random and systematic. The accuracy of any one result then, is a function of the bias (due to systematic error) and precision (due to random error) of the collection and analysis methodology. Bias has at least two components, associated with extraction and instrument efficiency, and is assessed by the mean recovery of Calibration Check Standards and Laboratory Control Standards (LCS). The LCS check overall bias for the system; the Calibration Check Standard determines the instrumental bias.

Total random error can be assessed by analyzing duplicate samples, but it includes errors due to sample collection, sample homogeneity, sample extraction, sample composition (matrix effects) and instrumental reproducibility. These errors can be evaluated by the use of the other QC procedures stated above and are assessed by calculating the standard deviations of the various analyses.

The accuracy of analysis, i.e., bias and precision, are evaluated separately below for the two types of samples, using the following equations:

$$\text{Recovery} = \text{Amount Found}/\text{Known Amount} \qquad (1)$$

$$\text{Bias (B)} = \text{Recovery} - 1. \qquad (2)$$

Difference (D) = $|x_1 - x_2|$ where x_1 and x_2 are the analytical results of paired analyses and the average is:

$$\bar{D} = \frac{\Sigma_i |x_1 - x_2|_i}{n} \tag{3}$$

and the precision is:

$$s_x = \text{Precision} = 0.8862\ \bar{D} \tag{4}$$

where 0.8862 converts the range of two results to the standard deviation (Natrella, 1963).

If component errors are used to assess total random error, then

$$\bar{D} = (\bar{D}_1 + \bar{D}_2 + \ldots)/n \text{ and} \tag{5}$$

$$s_x = \text{Precision} = [0.8862\ (\bar{D}_1^2 + \bar{D}_2^2 + \ldots) + s_1^2 + s_2^2 + \ldots]^{1/2}.$$

Equation (3) is suitable for use on results where the concentration varies over a very narrow range. If the concentrations found vary by an order of magnitude or more, then the difference should be normalized by dividing by the average of the two values and the precision is expressed as the coefficient of variation (CV) which is $s/\bar{x}$

$$\bar{D}_n = \frac{\Sigma}{n} \left(|x_1 - x_2|_i \right) \div \frac{(x_1 + x_2)i}{2} \tag{6}$$

$$2 \frac{\Sigma}{n} \frac{|x_1 - x_2|i}{(x_1 + x_2)i}$$

$$CV = 0.8862\ \bar{D}_n \tag{7}$$

One of the studies discussed by Brown and Black (1983) involved lead contaminated soils. The use and evaluation of the QC analyses for this soil monitoring study was presented as follows:

The limit of detection, approximately 0.25 $\mu g\ ml^{-1}$, was tested on about 10 blank analyses using a more sensitive absorbance wavelength for lead on an AAS. The result was less than 0.1 $\mu g\ ml^{-1}$, or 2 $\mu g\ g^{-1}$ for sample analysis. This suggests that most of the blank analyses were less than 2 $\mu g\ g^{-1}$, but this cannot be stated with any confidence. The results of the QC analyses were as follows:

QC Sample	No.	Mean	S
Calibration Check Standard	150	101.5%	2.6%
Laboratory Control Standard	147	101.2%	4.1%
Field Blank ($\mu g\ ml^{-1}$)	76	<0.25	
Sample Bank Blank ($\mu g\ ml^{-1}$)	77	<0.25	
Reagent Blank ($\mu g\ ml^{-1}$)	148	<0.25	
Re-extraction Analysis	17	1.7%	1.4%
Total Recoverable	144	99.8%	8.0%
Split Extract (CV)	147	0.0089	0.0079
Spiked Extract	147	99.4%	5.0%
Spiked Sample	147	100.4%	5.1%
Duplicate Aliquot(CV)	134	0.053	0.047
Duplicate Sample (CV)	129	0.189	0.168
Triplicate Analysis (CV)	220	0.144	0.128

(1) Bias: The percent recoveries indicated above for the Calibration Check Standards and LCS's suggest a small positive bias for the method of soil analysis, due principally to instrument reproducibility. The result, using Equation (2), is:

$$\text{Bias} = \text{Recovery} - 1 = 1.012 - 1 = 0.012.$$

(2) Precision: The recovery of the analyte by the analytical method compared to the "total" recoverable method was essentially equal and re-extraction of the residue left from the initial extraction indicated an additional 1.7 ± 1.4 percent recovery, also essentially equivalent. Furthermore, the results of the three types of blank analyses indicate no measurable contamination from reagents, sample collection, or sample preparation. The remaining random errors are evaluated below. Because of the wide range of concentration of lead in the samples, the coefficient of variation is used, Equation (7).

Precision (total random error) from Duplicate Sample Analysis:

CV = 0.168 or 16.8% of sample concentration.

The component random errors, summed as per Equation (5), are:

$$s_x = (0.0079^2 + 0.05^2 + 0.051^2 + 0.047^2)^{1/2} = 0.085.$$

These random errors suggest that reproducibility errors(0.0079) are small and that extract matrix, sample matrix, and sample homogeneity errors are equivalent. The sum of these errors is about half the total random error so the sampling error is essentially equal to all other errors combined.

Interlaboratory precision as calculated from the results of triplicate analyses, using Equation (7) is:

Precision = CV = 0.128 or 12.8% of sample concentration,

(3) Uncertainty: The data for bias and precision can be combined to yield the uncertainty for any reported concentration by use of the following equation:

$$U = (1 + B \pm 2\ C) \qquad (8)$$

where B is the bias, C is the standard deviation or coefficient of variation as appropriate, and 2 converts these to the 95 percent confidence limits. For soil analyses, using Equation (8) and the bias and CV derived above, the 95% confidence bounds on a reported value, x, are:

Soil result will lie between 0.676x and 1.348x $\mu g\ g^{-1}$.

It is required that the QA/QC plan ensure and document that all data collected, whether used for research or for monitoring purposes, is scientifically valid, defensible and of known precision and accuracy. The described presentation of QC data, though designed for analysis of lead in soil, can be used as a guide for other sampling and data analysis protocols and/or QA/QC plans.

Presentation of QA/QC data allows readers to verify conclusions drawn as to the reliability of the data. Such an approach also contributes to the building of a body of QA/QC and monitoring experimental data in the literature which allow comparisons to be made between and among studies. Procedures used to validate the individual data points should be presented and where some points are discarded arguments should be presented to support these decisions.

PRESENTATION OF RESULTS AND CONCLUSIONS

Special emphasis should be placed on how overall levels of precision and confidence were derived from the data. Great care must be exercised to insure that, in determining results and conclusions, assumptions are not made which were not part of the study design and which cannot be tested by data derived from the study. If portions of the study results are ambiguous and supportable conclusions cannot be drawn with regard to the total reliability of the data, that situation must be clearly stated. In that event it is desirable to include recommendations for conducting an improved study in such a way as to clarify the observed ambiguities.

QUALITY ASSURANCE ASPECTS

The adequacy of all aspects of the QA/QC plan should be examined in detail with emphasis on defining for future studies an appropriate minimum adequate plan. Some aspects of the plan actually used may have been too restrictive, some may not have been restrictive enough. Appropriate analyses and interpretation of the data should identify the actual situation.

Future soil monitoring studies should have checks and balances built into the QA/QC plan which will identify early in the study whether the plan is adequate and if necessary, allow for corrective action to be taken before the study continues. This is one of the major advantages of conducting an exploratory study along the lines outlined in this report. If there are problems with the QA/QC plan, they will often be identified in the exploratory study and be corrected before major resources are expended.

There is insufficient knowledge dealing with soil monitoring studies to state with confidence which portions of the QA/QC plan will be generally applicable to all soil monitoring studies and which portions must be varied depending on site-specific factors. As experience is gained, it may be possible to provide more adequate guidance on this subject. In the meantime it is recommended that the best approach is to assume that important factors of QA/QC plans are site-specific and to conduct an appropriate exploratory study at each new study site to verify that various aspects of the QA/QC plan are adequate to meet program objectives prior to proceeding with the final definitive study.

APPENDIX D

SYSTEM AUDITS AND TRAINING

INTRODUCTION

The material for this chapter has been obtained primarily from USEPA Kellogg Idaho Study (1984). The first phase of an auditing program for soil monitoring projects should be the preparation of standard operating procedures (SOP) that identify the methods and techniques necessary to perform all aspects of the required audit. The SOP must be adequate to perform onsite sampling and sample bank (where applicable) audits. The second phase should then be the actual conduct of the required field audit. Audits are conducted by appropriate elements of agencies or organizations having cognizance over the monitoring project. The frequency of auditing should be determined by the project officer. Juran et al. (1979) state that, "the activities subject to audit should include any that affect quality regardless of the internal organizational location."

A system audit is an overall evaluation of a project to:

- Verify that sampling methodology is being performed in accordance with program requirements
- Check on the use of appropriate QA/QC measures
- Check methods of sample handling, i.e., packaging, labeling, preserving, transporting, and archiving in accordance with progam requirements
- Identify any existing quality problems
- Check program documentation, i.e., records (site description, chain-of-custody collection and analytical tags, field and sample bank log books and field work sheets)
- Initiate corrective action if a problem is identified

- Assess personnel experience and qualifications if required

- Follow-up on any corrective action previously implemented

- Provide onsite debriefings for sampling team and sample bank personnel.

- Provide a written evaluation of the sampling and sample bank program

The purpose of the system audit is to ensure that the QA/QC system planned for the project is in place and functioning well.

The auditor first must review Work Plans, Protocols, Test Plans, QA/QC Project Plan, and all Program Reports. A discussion of the current status of the project, and the identity of any problems encountered, with the project officer is suggested before conducting the onsite sampling audit. Sample chain-of-custody procedures and raw data are checked as appropriate and results of blind QC samples routinely inserted in the sample load by sample bank personnel are reviewed. Spot-checks of sampling methods and techniques, sampling and analysis calculations, and data transcription are performed.

SAMPLE BANK AUDIT

The primary objective is to determine the status of all Sample Bank documentation and archived samples. Emphasis is placed on:

- Verifying that the documentation is in order and sufficient to establish the disposition of any sample collected

- Determining any discrepancies that currently exist and initiating corrective action as appropriate

- Verifying that the recording of QA/QC measures (blanks, duplicate spikes, blinds) is in accordance with the QA/QC Plan

- Establishing procedures for final disposition and mechanics of transfer of all Sample Bank holdings upon termination of the operation.

The first step of the audit is to inventory the Sample Bank records and archived samples. The records that must be inspected are:

- Chain-of-custody forms
  - Field forms
  - Analysis forms
- Sample tags
  - Field tags
  - Analysis tags
- Analysis forms
  - Individual samples
  - Batch sheets
- Shipment forms
- Logbooks
  - Soils
  - Daily log

The operational procedures inspected should include:

- Preparation Procedures (sample bank or analytical laboratory)
  - Drying (if used)
  - Sieving
  - Mixing
  - Packaging
  - Shipping
- Housekeeping
  - Safety
  - Decontamination
  - Evaluation of Swipe Samples
- Security
  - Forms (documents)
  - Samples
- Storage
  - Sampling equipment
  - Archived samples

Check that required documentation has been maintained in an orderly fashion, that each of the recorded items is properly categorized, and cross-checking can be easily performed. In addition, ensure that data recording conforms to strict document control protocols and the program's QA/QC Plan.

The archived samples inspected can be categorized as follows:

- Soil
- Blanks
- Splits
- Standard Reference Materials (SRM)
- Non-Soil Materials Collected with the Soil Sample

Conduct an audit of the archived samples. Verify that appropriate samples exist for each entry in the logbook. Field sample tags should be replaced by the appropriate analytical tags, and chain-of-custody forms are prepared in order to transfer the samples. Detailed sample bank procedures are presented by USEPA Dallas Lead Study (1984).

DAILY LOG

Check for clear, concise entries detailing events of the day (such as numbers of samples processed), problems encountered, and actions taken to solve them. This log can provide excellent documentation of the operation of the Sample Bank.

SAMPLE BANK LOGS

Review these logs for complete sample information entered. Changes made should be by crossing out so the original entry is still visible, and initialing. In addition checks for the identification and documentation of split and duplicate samples, and field and Sample Bank blanks must be performed.

SAMPLE COLLECTION AUDITS

It is recommended that an audit of the overall QA/QC plan for sample documentation, collection, preparation, storage, and transfer procedures be performed just before sampling starts. The intent of this audit is to critically review the entire sampling operation to determine the need for any corrective action early in the program. Additional total program or partial audits can be conducted at various times throughout the sampling program.

It is recommended that the Project Officer maintain a QA/QC Coordinator onsite during sample collection to monitor the sampling team's activities, provide technical and corrective action suggestions to the sampling teams, and supplement performance audits on sampling as needed.

FIELD AUDITS

The primary objective is to determine the status of sampling operations. Emphasis is placed on:

- Verifying that operational aspects and procedures are in accordance with the protocols and QA/QC plan.
- Verifying the collection of all samples including duplicates and field blanks.
- Verifying that documentation is in order and sufficient to establish the collection location of any sample collected.
- Determining discrepancies that exist and initiating corrective action as appropriate.
- Collecting independent samples.

The on-site field audit is to inspect sample records and equipment. Records inspected include:

a. Chain-of-Custody Forms

b. Sample Tags

c. Site Description Forms

d. Log Books

The operational procedures inspected should include:

- Sampling Procedures
    - Equipment
    - Techniques
    - Decontamination
    - Collection of duplicate and field blank samples
    - Security
    - Sample storage and transportation
    - Containers
    - Contaminated waste storage and disposal
    - Site Description Form entries

DATA MANAGEMENT AUDITS

An audit of the data management system by tracing the flow of specific samples through the system should be performed. In particular, the ability of the system to correctly identify a sample from any one of its identification numbers should be checked.

Entries in the sample bank's logbook will be the basis for these performance checks. From time to time, erroneous input information may be used to audit the system.

TRAINING

The project leader of a soil monitoring project is responsible for ascertaining that all members of his project team have adequate training and experience to carry out satisfactorily their assigned missions and functions. Until a field sampling team has worked together long enough for the project leader to have verified this from first hand knowledge it is good practice, in addition to any classroom training or experience, to conduct comprehensive briefing sessions for all involved parties during which all aspects of the sampling protocol, including the QA/QC plan, are presented and discussed in some detail. This approach will help the project personnel to develop into a team where each team member knows his own job well and knows how it fits into the overall team effort. Sufficient field training exercises should follow the briefing sessions until each team member can demonstrate successfully that he can perform his job routinely well and without delay. Of course, on subsequent projects of the same general type with the same team, the training exercises may be reduced in number or dispensed with as deemed appropriate by the project leader.

In summary, the sampling effort must include classroom and field training programs that have provided detailed instruction and practical experience to personnel in sample collection techniques and procedures, labeling, preservation, documentation, transport, and sample bank operational procedures. Also, special training programs concerning procedures and program documentation should be completed by all personnel prior to their involvement in the conduction of any audits.